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* * * * * * * * * *   Welcome to STN International   * * * * * * * * * *

 NEWS  1          Web Page for STN Seminar Schedule - N. America
 NEWS  2  DEC 01  ChemPort single article sales feature unavailable
 NEWS  3  APR 03  CAS coverage of exemplified prophetic substances
                  enhanced
 NEWS  4  APR 07  STN is raising the limits on saved answers
 NEWS  5  APR 24  CA/CAplus now has more comprehensive patent assignee
                  information
 NEWS  6  APR 26  USPATFULL and USPAT2 enhanced with patent
                  assignment/reassignment information
 NEWS  7  APR 28  CAS patent authority coverage expanded
 NEWS  8  APR 28  ENCOMPLIT/ENCOMPLIT2 search fields enhanced
 NEWS  9  APR 28  Limits doubled for structure searching in CAS
                  REGISTRY
 NEWS 10  MAY 08  STN Express, Version 8.4, now available
 NEWS 11  MAY 11  STN on the Web enhanced
 NEWS 12  MAY 11  BEILSTEIN substance information now available on
                  STN Easy
 NEWS 13  MAY 14  DGENE, PCTGEN and USGENE enhanced with increased
                  limits for exact sequence match searches and
                  introduction of free HIT display format
 NEWS 14  MAY 15  INPADOCDB and INPAFAMDB enhanced with Chinese legal
                  status data
 NEWS 15  MAY 28  CAS databases on STN enhanced with NANO super role in
                  records back to 1992
 NEWS 16  JUN 01  CAS REGISTRY Source of Registration (SR) searching
                  enhanced on STN
 NEWS 17  JUN 26  NUTRACEUT and PHARMAML no longer updated
 NEWS 18  JUN 29  IMSCOPROFILE now reloaded monthly
 NEWS 19  JUN 29  EPFULL adds Simultaneous Left and Right Truncation
                  (SLART) to AB, MCLM, and TI fields
 NEWS 20  JUL 09  PATDPAFULL adds Simultaneous Left and Right
                  Truncation (SLART) to AB, CLM, MCLM, and TI fields

 NEWS EXPRESS MAY 26 09 CURRENT WINDOWS VERSION IS V8.4,
              AND CURRENT DISCOVER FILE IS DATED 06 APRIL 2009.

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FILE 'HOME' ENTERED AT 13:53:11 ON 09 JUL 2009

=> file reg
COST IN U.S. DOLLARS                                 SINCE FILE      TOTAL
                                                        ENTRY    SESSION
FULL ESTIMATED COST                                      0.66       0.66

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DICTIONARY FILE UPDATES: 8 JUL 2009 HIGHEST RN 1161500-61-3

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=>
Uploading C:\Program Files\Stnexp\Queries\10580384.str

L1   STRUCTURE UPLOADED

=> d l1
L1 HAS NO ANSWERS
L1   STR

Structure attributes must be viewed using STN Express query preparation.

=> s l1
SAMPLE SEARCH INITIATED 13:55:21 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -   13525 TO ITERATE

 14.8% PROCESSED   2000 ITERATIONS   50 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS: 263531 TO   277469
PROJECTED ANSWERS: 90284 TO   98524

L2   50 SEA SSS SAM L1

=> s l1 full
FULL SEARCH INITIATED 13:55:25 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -   273365 TO ITERATE

100.0% PROCESSED   273365 ITERATIONS   94871 ANSWERS
SEARCH TIME: 00.00.02

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L3        94871 SEA SSS FUL L1

=> file caplus
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                      ENTRY    SESSION
FULL ESTIMATED COST                                  185.88     186.54

FILE 'CAPLUS' ENTERED AT 13:55:31 ON 09 JUL 2009
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FILE COVERS 1907 - 9 Jul 2009  VOL 151 ISS 2
FILE LAST UPDATED: 8 Jul 2009  (20090708/ED)
REVISED CLASS FIELDS (/NCL) LAST RELOADED:  Apr 2009
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE:  Apr 2009

CAplus now includes complete International Patent Classification (IPC)
reclassification data for the second quarter of 2009.

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This file contains CAS Registry Numbers for easy and accurate
substance identification.

=> s l3
L4        31119 L3

=> s l4 and acrylic
         316082 ACRYLIC
L5         1508 L4 AND ACRYLIC

=> s l4 and methacrylic
          88473 METHACRYLIC
L6          503 L4 AND METHACRYLIC

=> s l4 and (meth)acrylic
MISSING OPERATOR METH)ACRYLIC
The search profile that was entered contains terms or
nested terms that are not separated by a logical operator.

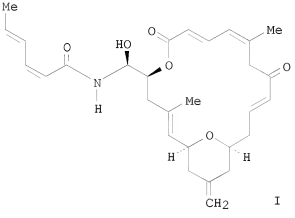
=> s l5 or l6
L7         1685 L5 OR L6

=> s l7 and esterification
         108157 ESTERIFICATION
L8           25 L7 AND ESTERIFICATION

=> d l8 ibib abs 1-
```

YOU HAVE REQUESTED DATA FROM 25 ANSWERS - CONTINUE? Y/(N):y

L8 ANSWER 1 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2008:1032796 CAPLUS
DOCUMENT NUMBER: 150:374168
TITLE: Studies toward the synthesis of (-)-zampanolide: preparation of the macrocyclic core
AUTHOR(S): Troast, Dawn M.; Yuan, Jiayi; Porco, John A., Jr.
CORPORATE SOURCE: Department of Chemistry, Center for Chemical Methodology and Library Development (CMLD-BU), Boston University, Boston, MA, 02215, USA
SOURCE: Advanced Synthesis & Catalysis (2008), 350(11+12), 1701-1711
CODEN: ASCAF7; ISSN: 1615-4150
PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 150:374168
GI



I

AB Studies towards the synthesis of the macrocyclic core of (-)-zampanolide (I) are reported. The synthetic approach features a one-pot reduction/vinylogous aldol reaction for construction of the C-15-C-20 fragment, an intramol. silyl-modified Sakurai (ISMS) reaction for construction of the 2,6-cis-disubstituted exo-methylene pyran subunit, and use of an sp2-sp3 Stille reaction for macrocyclization.
REFERENCE COUNT: 102 THERE ARE 102 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 2 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2006:718802 CAPLUS
DOCUMENT NUMBER: 145:335974
TITLE: SuperQuat 5,5-dimethyl-4-iso-propyloxazolidin-2-one as a mimic of Evans 4-tert-butyloxazolidin-2-one
AUTHOR(S): Bull, Steven D.; Davies, Stephen G.; Garner, A. Christopher; Kruchinin, Dennis; Key, Min-Suk; Roberts, Paul M.; Savory, Edward D.; Smith, Andrew D.; Thomson, James E.
CORPORATE SOURCE: The Department of Organic Chemistry, Chemistry Research Laboratory, University of Oxford, Oxford, OX1 3TA, UK

SOURCE: Organic & Biomolecular Chemistry (2006), 4(15), 2945-2964
CODEN: OBCRAK; ISSN: 1477-0520
PUBLISHER: Royal Society of Chemistry
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 145:335974

AB The incorporation of a gem-di-Me group at the 5-position of a chiral oxazolidinone biases the conformation of the adjacent C(4)-stereodirecting group such that the gem-dimethyl-4-iso-Pr combination mimics a C(4)-tert-Bu group, providing higher levels of stereocontrol than a simple 4-isopropyloxazolidinone. The stereoselectivities of alkylation, esterification (O-acylation), Diels-Alder, and alkene oxidative acetalization reactions of acyloxazolidinones with either a 4-iso-Pr or 4-tert-Bu group and either possessing or lacking gem-5,5-dimethyl groups are compared.

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 3 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2005:822461 CAPLUS
DOCUMENT NUMBER: 143:212623
TITLE: Crosslinking of compounds having hydroxy groups bonded to aromatic rings and the crosslinked products
INVENTOR(S): Morita, Takehiko; Tsujino, Naoshi
PATENT ASSIGNEE(S): Nippon Shokubai Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 13 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2005220221	A	20050818	JP 2004-29250	20040205

PRIORITY APPLN. INFO.: JP 2004-29250 20040205

AB Aromatic compds. having ≥1 OH and (meth)acryloyloxy or (meth)acryloyloxyalkoxy groups on the same aromatic ring are allowed to react with compds. having oxazoline, epoxy, and/or isocyanate groups. Thus, a mixture of 2-isopropenyl-2-oxazoline 20, Me methacrylate 50, Bu acrylate 20, 2-(2-acryloyloxyethoxy)phenol (preparation decribed) 10, and AIBN 1.5 parts was added dropwise to EtOAc at 80° for 4 h, heated to 90° for 2.5 h, and cooled to give a solution of a prepolymer having phenolic OH and oxazoline groups, which was mixed with 0.1 phr di-Ph phosphite, applied on a glass sheet, and crosslinked at 180° for 1 h to form a water-resistant coating.

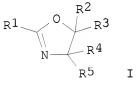
L8 ANSWER 4 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2005:472105 CAPLUS
DOCUMENT NUMBER: 143:8161
TITLE: Method for the esterification of alcohols with olefinically unsaturated carboxylic acids
INVENTOR(S): Glos, Martin
PATENT ASSIGNEE(S): Clariant G.m.b.H., Germany
SOURCE: PCT Int. Appl., 20 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE

WO 2005049544	A1	20050602	WO 2004-EP12790	20041111
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 10354652	A1	20050707	DE 2003-10354652	20031122
AU 2004291298	A1	20050602	AU 2004-291298	20041111
CA 2546819	A1	20050602	CA 2004-2546819	20041111
EP 1687251	A1	20060809	EP 2004-797820	20041111
EP 1687251	B1	20090318		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS				
BR 2004016734	A	20070116	BR 2004-16734	20041111
CN 1902155	A	20070124	CN 2004-80030595	20041111
JP 2007511561	T	20070510	JP 2006-540260	20041111
ES 2320227	T3	20090520	ES 2004-797820	20041111
MX 2006005674	A	20060817	MX 2006-5674	20060519
US 20070149803	A1	20070628	US 2006-580384	20060522
PRIORITY APPLN. INFO.:			DE 2003-10354652 A	20031122
			WO 2004-EP12790 W	20041111

OTHER SOURCE(S): MARPAT 143:8161

GI



I

AB The invention relates to a method for producing esters from alcs. and olefinically unsatd. carboxylic acids by reacting an alc. with an olefinically unsatd. carboxylic acid or a reactive derivative thereof, in the presence of between 1 ppm and 1 weight % oxazoline I in relation to the weight of the reaction mixture of alc. and olefinically unsatd. carboxylic acid/carboxylic acid derivative, R1, R2, R3, R4 and R5 representing hydrogen or branched, linear, cyclical, saturated or unsatd. hydrocarbon radicals containing up to 25 C atoms that can be substituted by heteroatoms, and R1, R2, R3, R4 and R5 being the same or different to prevent formation of polymer on surfaces in reactor.

REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 5 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2004:651161 CAPLUS

DOCUMENT NUMBER: 141:175121

TITLE: Transparent scratch-resistant laminated polyester film

INVENTOR(S): Tojo, Mitsumine

PATENT ASSIGNEE(S): Teijin Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 13 pp.
CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2004223938	A	20040812	JP 2003-15745	20030124

PRIORITY APPLN. INFO.: JP 2003-15745 20030124

AB The laminated film, useful for an optical film, has thickness 20-300 μm and comprises a polyester substrate layer having at least thereon a coating layer, wherein (i) the substrate layer is substantially free from particles and the coating layer contains inert particles with mean particle diameter 10-150 nm and (ii) the substrate layer contains cyclic trimer ≤0.8% and concentration of terminal carboxyl group of the polymer ≤30 equiv/106 g. Thus, poly(ethylene terephthalate) with intrinsic viscosity 0.60, prepared by esterification, GeO2-catalyzed polycondensation, and solid-phase polymerization of bis(β-hydroxyethyl) terephthalate, terephthalic acid, and ethylene glycol at parts ratio 100:65:29, was brought into contact with hot water (90°), dried, extruded at 295°, quenched on a drum to give an undrawn film, and stretched 3.6-folds at 100° in the machine direction to give a uniaxially drawn substrate film. A coating containing 78 parts 90:5:5:90:50 (mol%) di-Me 2,6-naphthalenedicarboxylate-dimethyl isophthalate-dimethyl 5-sodiosulfoisophthalate-ethylene glycol-diethylene glycol copolymer, 15 parts 10:70:5:15 (mol%) Me methacrylate-2-isopropenyl-2-oxazoline-poly(ethylene oxide) methacrylate-acrylamide copolymer, 2 parts SiO2 (Cataloid Si 80p), and 5 parts Naroacty N 70 (polyoxyethylene lauryl ether) was applied on the substrate film, stretched 3.8-folds in the transverse direction at 110°, and set at 215° to give a 100-μm thick film with total light transmittance 92%, haze ≤0.8%, and good resistances to scratch and heat.

L8 ANSWER 6 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2001:417041 CAPLUS
DOCUMENT NUMBER: 135:34551
TITLE: Hydrophilic hydrogel-forming polymers comprising 1,4-α-D-glycosidic bonds
INVENTOR(S): Engelhardt, Friedrich; Frenz, Volker; Herfert, Norbert; Riegel, Ulrich; Weismantel, Matthias
PATENT ASSIGNEE(S): Basf Aktiengesellschaft, Germany
SOURCE: PCT Int. Appl., 28 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001040335	A1	20010607	WO 2000-EP11276	20001115

W: BR, CA, JP, MX
RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR

PRIORITY APPLN. INFO.: US 1999-450948 A 19991129

AB The title polymers comprising 1,4-α-D-glycosidic bonds and acid groups and/or their alkali or ammonium salts are post-crosslinked on the surface and have (a) a centrifuge retention capacity (CRC) parameter of 1.10 and (b) a vertical absorption (test description given) of <12 g/g. The polymers have good absorptive power and retention of liqs. and are useful for the manufacture of diapers and related articles. For example, redox polymerization of acrylic acid and methylenebisacrylamide copolymer in the presence of starch allyl ether as crosslinker (preparation given) gave a solid gel which was comminuted, partly neutralized with aqueous NaOH, dried

and surface-modified with diglycidyl propylphosphonate and ethylene glycol diglycidyl ether to give a title hydrogel having CRC parameter 1.293 and vertical absorption 12.5 g/g.
REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 7 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2000:153666 CAPLUS
DOCUMENT NUMBER: 132:279065
TITLE: Ruthenium Carbene Complexes with N,N'-Bis(mesityl)imidazol-2-ylidene Ligands: RCM Catalysts of Extended Scope
AUTHOR(S): Fuerstner, Alois; Thiel, Oliver R.; Ackermann, Lutz; Schanz, Hans-Joerg; Nolan, Steven P.
CORPORATE SOURCE: Max-Planck-Institut fuer Kohlenforschung, Muelheim/Ruhr, D-45470, Germany
SOURCE: Journal of Organic Chemistry (2000), 65(7), 2204-2207 CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 132:279065
AB The Ru carbene complexes Cl2Ru(PCy3)L(L') 3a,b (L = N,N'-dimesityl-2,3-dihydro-1H-imidazol-2-ylidene; L' = benzylidene, 3-phenylindenylidene) constitute excellent precatalysts for ring-closing metathesis (RCM) reactions allowing the formation of tri- and tetrasubstituted cycloalkenes (e.g. 3,4-dimethyl-3-cyclopentene-1,1-dicarboxylic acid di-Et ester). They also apply to annulations that are beyond the scope of the standard Grubbs carbene Cl2Ru(PCy3)2(:CHPh) (e.g. 1,2,3,4,5,6-hexahydroindene-3a-carboxylic acid Me ester) as well as to ring-closing reactions of acrylic acid derivs. even if the resulting α,β-unsatd. lactones (or lactams) are tri- or tetrasubstituted (e.g. 5-ethyl-3,4-dimethyl-2(5H)-furanone). The reactivity of 3a is highly dependent on the reaction medium: particularly high reaction rates are observed in toluene, although this solvent also leads to an increased tendency of the catalyst to isomerize the double bonds of the substrates.
REFERENCE COUNT: 52 THERE ARE 52 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 8 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1996:243094 CAPLUS
DOCUMENT NUMBER: 125:34317
ORIGINAL REFERENCE NO.: 125:6721a,6724a
TITLE: FTIR spectroscopic studies on the interfacial reactions of oxazoline-functionalized polymers
AUTHOR(S): Schaefer, R.; Kressler, J.; Muelhaupt, R.
CORPORATE SOURCE: Inst. Makromol. Chem., Albert-Ludwigs-Univ., Freiburg, D-79104, Germany
SOURCE: Acta Polymerica (1996), 47(4), 170-6 CODEN: ACPODY; ISSN: 0323-7648
PUBLISHER: VCH
DOCUMENT TYPE: Journal
LANGUAGE: English
AB The interfacial reaction of immiscible polymeric systems containing oxazoline and carboxylic acid groups, resp., was studied by FTIR spectroscopy and FTIR microscopy. A butadiene-acrylonitrile copolymer rubber, where the nitrile groups were partially converted to oxazoline groups, was thermally annealed in a 2-layer specimen with ethene-methacrylic acid copolymer (PEM). The formation of the ester amide in the interface was measured quant. by FTIR difference spectroscopy. Evaluating the formation of the amide I band led to reaction rate consts. of 0.0125-0.022 s-1 at 170-230°. This system was immiscible because there is no

interdiffusion across the interface. Also, the formation of an ester amide in the interfacial reaction of the system PEM/bis(1,3-oxazoline-2-yl)-terminated di-Me siloxane was monitored qual. by FTIR spectroscopy.

L8 ANSWER 9 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1994:108707 CAPLUS
DOCUMENT NUMBER: 120:108707
ORIGINAL REFERENCE NO.: 120:19211a,19214a
TITLE: Methacryloxyethyl vinyl carbonate as novel UV-curable crosslinking agent for acrylic, vinyl, and styrenic hydrophilic monomers
INVENTOR(S): Lai, Yu Chin
PATENT ASSIGNEE(S): Bausch and Lomb Inc., USA
SOURCE: PCT Int. Appl., 101 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9309084	A1	19930513	WO 1992-US9539	19921103
W: AU, BR, CA, JP, KR				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE				
US 5310779	A	19940510	US 1992-922452	19920730
AU 9230664	A	19930607	AU 1992-30664	19921103
AU 664401	B2	19951116		
EP 611367	A1	19940824	EP 1992-924307	19921103
EP 611367	B1	19970625		
R: BE, DE, ES, FR, GB, GR, IE, IT, NL, SE				
JP 07500865	T	19950126	JP 1992-508729	19921103
BR 9206886	A	19950411	BR 1992-6886	19921103
CA 2121577	C	20000620	CA 1992-2121577	19921103
JP 3490436	B2	20040126	JP 1993-508729	19921103
IN 186331	A1	20010811	IN 1992-DE1017	19921105

PRIORITY APPLN. INFO.:
US 1991-788071 A 19911105
US 1992-884481 A 19920515
US 1992-922452 A 19920730
WO 1992-US9539 A 19921103

AB UV-cured hydrogels prepared by polymerizing ≥1 (meth)acrylate- or (meth)acrylamide-capped urethane-siloxane macromer of specified structure, ≥1 vinyl monomer, e.g., N-vinylpyrrolidone, and ≥1 crosslinking agent of specified structure, e.g. methacryloxyethyl vinyl carbonate (I), -carbamate, or -urea, 4-vinylphenyl vinyl urea, etc., are useful for the manufacture of biomedical devices, especially contact lenses. Thus, a mixture of α,ω-bis(methacryloxybutyl)polysiloxane 13, 3-methacryloxypropyl tris(trimethylsiloxy)silane 47, N-vinylpyrrolidone 40, I (preparation from CH2:CMeCO2CH2CH2OH and ClCO2CH:CH2 given) 0.1, Darocur 1173 0.2, and benzoin Me ether 0.2 parts in hexanol was cast onto a glass plate, UV-cured, extracted, and equilibrated in buffered saline at pH 7.4 to give a film containing 23% H2O and having modulus 369 g/mm2, contact angle 20°, and O permeability 114 Dk units.

REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

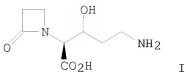
L8 ANSWER 10 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1993:628125 CAPLUS
DOCUMENT NUMBER: 119:228125
ORIGINAL REFERENCE NO.: 119:40695a,40698a
TITLE: Low loss high numerical aperture cladded optical

fibers
INVENTOR(S): Babirad, Stefan A.; Kuczma, Andrew S.; Savu, Patricia M.
PATENT ASSIGNEE(S): Minnesota Mining and Manufacturing Co., USA
SOURCE: PCT Int. Appl., 35 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9304132	A1	19930304	WO 1992-US5976	19920716
W: CA, JP, KR				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE				
US 5239026	A	19930824	US 1991-750092	19910826
EP 600985	A1	19940615	EP 1992-917902	19920716
EP 600985	B1	19970115		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, MC, NL, SE				
JP 06510316	T	19941117	JP 1992-504296	19920716
JP 2756188	B2	19980525		
ES 2096098	T3	19970301	ES 1992-917902	19920716
CA 2114796	C	20030513	CA 1992-2114796	19920716
PRIORITY APPLN. INFO.:			US 1991-750092 A	19910826
			WO 1992-US5976 W	19920716

AB The title optical fibers are prepared by coating with compns. containing fluorinated monoacrylates, fluorinated polyvinyl compds., adhesion-promoting monomers and optionally silane-free fluorinated acrylamides, non-fluorinated mono or polyvinyl compds., non-fluorinated silanes, photoinitiators, thermal stabilizers, and antioxidants. Thus, a composition containing (perfluorocyclohexyl)methyl acrylate, trimethoxysilylpropyl methacrylate, hexafluoropentamethylene diacrylate, stabilizers and an initiator gave a 25-μm cladding on an optical fiber and showed optical loss 3.8 dB/km and numerical aperture 0.45 (at 633 nm for a 2-m fiber).
REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 11 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1991:6078 CAPLUS
DOCUMENT NUMBER: 114:6078
ORIGINAL REFERENCE NO.: 114:1195a,1198a
TITLE: Studies on the biosynthesis of clavulanic acid. Part 5. Absolute stereochemistry of proclavaminic acid, the monocyclic biosynthetic precursor of clavulanic acid
AUTHOR(S): Baggaley, Keith H.; Elson, Stephen W.; Nicholson, Neville H.; Sime, John T.
CORPORATE SOURCE: Chemother. Res. Cent., Beecham Pharm., Betchworth/Surrey, RH3 7AJ, UK
SOURCE: Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1990), (6), 1521-33
CODEN: JCPRB4; ISSN: 0300-922X
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 114:6078
GI



I

AB Proclayaminic acid was synthesized by a route which indicated its constitution to be (2S,3R)-5-amino-3-hydroxy-2-(2-oxoazetidin-1-yl)valeric acid (I). The spectroscopic properties of synthetic I were identical with those of natural I and both were converted into clavaminic acid by clavaminic acid synthase. An efficient synthesis of 3-hydroxyornithine derivs. was devised which allowed the separation of diastereoisomers and the resolution of a threo compound by the acylase [EC 3.5.1.11] from Escherichia coli. The β-lactam ring was subsequently elaborated by Michael addition of a protected 3-hydroxyornithine to acrylic acid followed by ring closure using PPh3-di-2-pyridyl disulfide. Model reactions were carried out with enantiomerically pure threonine derivs. to confirm that the formation of the β-lactam moiety did not impair the integrity of the α- and β-chiral centers and that the enzymic deacylation reaction was capable of resolving the α-center of an α-amino-β-hydroxy acid. The enantiomeric purity of intermediates was determined using HPLC, 1H NMR spectroscopy utilizing the chiral solvating reagents (R)- and (S)-1-(9-anthryl)-2,2,2-trifluoroethanol, and chiral GLC techniques.

L8 ANSWER 12 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1989:477514 CAPLUS
DOCUMENT NUMBER: 111:77514
ORIGINAL REFERENCE NO.: 111:13055a,13058a
TITLE: Purification of unsaturated carboxylic acid isocyanatoalkyl esters by distillation
INVENTOR(S): Abe, Tetsuo; Yokoo, Hidejiro; Nozawa, Kaneo
PATENT ASSIGNEE(S): Showa Rodia Kagaku Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 01042461	A	19890214	JP 1987-198155	19870810
JP 07049413	B	19950531		
PRIORITY APPLN. INFO.:			JP 1987-198155	19870810

OTHER SOURCE(S): MARPAT 111:77514
AB The title esters, useful as monomers, are purified by distillation under continuous or intermittent addition of nitrite esters in the presence of Sn(2+) and/or Fe(2+) compds. to prevent popcorn polymerization CH2:CMeCO2H (320 g) was gradually added to a solution of 300 g 2-oxazolidinone in toluene containing phenothiazine while bubbling with HCl at 60° over 60 min, and the reaction mixture was further bubbled with HCl at 60° for 30 min, and then heated at 80° while bubbling with COCl2. After distilling off toluene, 230 g product containing CH2:CMeCO2CH2CH2NCO (I) was distilled with SnCl2 and the HNO2 ester (II) of HOCH2CH2OCH2CH2OBu under dropwise addition of 50 g product containing II to give 115 g I. When the reaction product was distilled without addition of SnCl2 and II, granules of polymerized matter were formed at the upper part of the distillation tower and polymer beads grew in the reaction mixture

L8 ANSWER 13 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1989:441476 CAPLUS
DOCUMENT NUMBER: 111:41476
ORIGINAL REFERENCE NO.: 111:7051a,7054a
TITLE: Silyl-containing vinyl resin compositions for coatings
INVENTOR(S): Yamashita, Takeshi; Konno, Eiju
PATENT ASSIGNEE(S): Dainippon Ink and Chemicals, Inc., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63275679	A	19881114	JP 1987-109898	19870507

PRIORITY APPLN. INFO.: JP 1987-109898 19870507

AB Storage-stable title compns. comprise polyoxazolines and vinyl polymers prepared from 1-100% vinyl monomers containing ≥1 unsatd. double bond and silyl ester group and 0-99% other vinyl monomers. Thus, styrene 200, Bu methacrylate 443, Acriester SL 150, and trimethylsilyl methacrylate 207 parts were polymerized in xylene in the presence of tert-Bu peroxyoctoate to give a polymer (I, number-average mol. weight 13,000) solution A mixture of the solution 100, 1,3-bis(A2-oxazolin-2-yl)benzene 7.7, and HC(OMe)3 2.0 parts was diluted to give a storage-stable composition, which was sprayed on a Zn3(PO4)2-treated steel plate and heated 30 min at 160° to form a coating with pencil hardness F-H, impact resistance 50, and good alkali, acid, and solvent resistance, vs., F-H, 20, poor, poor, and poor, resp., for a coating containing I (number-average mol. weight 850).

L8 ANSWER 14 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1989:173884 CAPLUS
DOCUMENT NUMBER: 110:173884
ORIGINAL REFERENCE NO.: 110:28867a,28870a
TITLE: End capping of growing species of poly(2-oxazoline) with carboxylic acid: a novel and convenient route to prepare vinyl- and carboxy-terminated macromonomers
AUTHOR(S): Miyamoto, Masatoshi; Naka, Kensuke; Tokumizu, Makoto; Saegusa, Takeo
CORPORATE SOURCE: Dep. Synth. Chem., Kyoto Univ., Kyoto, 606, Japan
SOURCE: Macromolecules (1989), 22(4), 1604-7
CODEN: MAMOBX; ISSN: 0024-9297
DOCUMENT TYPE: Journal
LANGUAGE: English

AB End-capping esterification of the growing oxazolinium end group in the polymerization of 2-oxazolines (2-Me and 2-Et derivs.) was accomplished by the binary system of carboxylic acid and a proton scavenger of hindered base such as 2,6-lutidine. Reaction conditions for complete and quant. end capping were established. The methodol. was successfully applied to the synthesis of macromonomers having an acrylate end group (end capping with acrylic acid) and having a carboxylic acid end group (end capping with a dibasic acid). In addition, an A-B-A-type block copolymer between poly[(N-acylimino)ethylene] and poly(oxyethylene) was readily prepared by using poly(oxyethylene) dicarboxylic acid.

L8 ANSWER 15 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1988:168145 CAPLUS
DOCUMENT NUMBER: 108:168145
ORIGINAL REFERENCE NO.: 108:27663a,27666a
TITLE: Preparation of unsaturated fatty acid

2-isocyanatoethyl esters from 2-oxazolidinone, unsaturated fatty acids, and phosgene
INVENTOR(S): Yokoo, Hidejiro
PATENT ASSIGNEE(S): Showa Rhodia Kagaku Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 2
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 63010750	A	19880118	JP 1986-152782	19860701
JP 07042263	B	19950510		
PRIORITY APPLN. INFO.:			JP 1986-152782	19860701

OTHER SOURCE(S): CASREACT 108:168145
AB Unsatd. lower fatty acid 2-isocyanatoethyl esters, useful as bifunctional monomers, were prepared by treating 2-oxazolidinone (I) with unsatd. fatty acids in the presence of HCl followed by treatment of the resulting product with COCl2. Thus, 32 g CH2:CMeCO2H was added dropwise to a toluene solution containing 30 g I and phenothiazine under bubbling with HCl at 60° over 60 min, the reaction mixture was further stirred under HCl for 30 min, and then the resulting suspension was bubbled with COCl2 at 80° till it became homogeneous solution to give 24 g CH2:CMeCO2CH2CH2NCO.

L8 ANSWER 16 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1987:618053 CAPLUS
DOCUMENT NUMBER: 107:218053
ORIGINAL REFERENCE NO.: 107:35007a,35010a
TITLE: Fixation of lysine by its α-amino function to oligomethacrylic chains
AUTHOR(S): Laguerre, A.; Rabadeux, J. C.; Gueniffey, H.; Bruneau, C. M.
CORPORATE SOURCE: Fac. Sci., Univ. Maine Route, Laval, 72017, Fr.
SOURCE: European Polymer Journal (1987), 23(2), 113-16
CODEN: EUPJAG; ISSN: 0014-3057
DOCUMENT TYPE: Journal
LANGUAGE: French
AB The title fixation was achieved via treatment of oligomethacrylate chloroformate with H-Lys(CO2CH2Ph)-OMe.

L8 ANSWER 17 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1985:221648 CAPLUS
DOCUMENT NUMBER: 102:221648
ORIGINAL REFERENCE NO.: 102:34793a,34796a
TITLE: Vinyl ester resins containing triazine or both triazine and oxazoline groups
INVENTOR(S): Hefner, Robert E., Jr.
PATENT ASSIGNEE(S): Dow Chemical Co., USA
SOURCE: U.S., 12 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 4515934	A	19850507	US 1984-590819	19840319
WO 8504176	A1	19850926	WO 1984-US1725	19841025
W: AU, BR, DK, FI, JP, KR, NO				

AU 8435567	A	19851011	AU 1984-35567		19841025
AU 555851	B2	19861009			
BR 8407303	A	19860325	BR 1984-7303		19841025
JP 61501396	T	19860710	JP 1984-504017		19841025
JP 03057930	B	19910903			
CA 1235845	A1	19880426	CA 1984-466386		19841026
EP 156959	A1	19851009	EP 1984-113039		19841030
EP 156959	B1	19890125			
R: AT, BE, CH, DE, FR, GB, IT, LI, NL, SE					
ZA 8408471	A	19860625	ZA 1984-8471		19841030
IL 73357	A	19880531	IL 1984-73357		19841030
AT 40391	T	19890215	AT 1984-113039		19841030
FI 8504184	A	19851025	FI 1985-4184		19851025
FI 81108	B	19900531			
FI 81108	C	19900910			
NO 8504596	A	19851118	NO 1985-4596		19851118
NO 162245	B	19890821			
NO 162245	C	19891129			
DK 8505339	A	19851119	DK 1985-5339		19851119
PRIORITY APPLN. INFO.:			US 1984-590819	A	19840319
			WO 1984-US1725	A	19841025
			EP 1984-113039	A	19841030

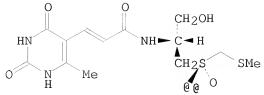
AB Heat-resistant vinyl ester resins are manufacture by esterification of aromatic epoxy resins containing oxazoline and (or) triazine groups with monounsatd. monoacids. Thus, 75.9 g Et3N was added in 20 min to 87.39 g CNBr and 342.45 g bisphenol A (I) in 950 mL Me2CO at -5 to -1°, and the reaction mixture was held 30 mins at -3 to +5° to give 337 g product mixture containing I 59.53, I monocyanate 35.01, and I dicyanate 5.46% , which was trimerized (335 g) 1.25 h at 177° in presence of 0.34 g 6% Co naphthenate to give a transparent, triazine ring-containing oligomer. This oligomer (250 g) was epoxidized with 763.05 g epichlorohydrin in 410.87 g iso-PrOH and 66.35 g water at 50-60° in presence of 171.53 g NaOH (added as a solution in 686.11 g water in 2 steps) to give a resin with epoxide equivalent weight 193.43. This resin (300 g) was esterified with 129.38 g methacrylic acid in presence of 0.172 g hydroquinone and 0.375 g CrCl3 catalyst (added as a 33.33% aqueous solution) at 90-117° to give a vinyl ester resin containing 1.298% carboxylic acid, which was mixed with 0.172 g phenothiazine, 240.63 g styrene, 1% Bz2O2, and 0.05% PhNMe2, cured at room temperature 24 h after cure exotherm subsided, and post cured 2 h at 100° to give a cast molding with heat-distortion temperature 105.5° and tensile strength 64.1 kPa, compared with 101.1 and 62.1, resp. , for a molding prepared from a methacrylated mixture of epoxy novolak resin and I diglycidyl ether.

REFERENCE COUNT: 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

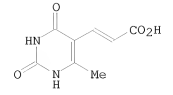
L8 ANSWER 18 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER:	1981:480671 CAPLUS
DOCUMENT NUMBER:	95:80671
ORIGINAL REFERENCE NO.:	95:13639a,13642a
TITLE:	Total synthesis of the antibiotic sparsomycin, a modified uracil amino acid monoxodithioacetal
AUTHOR(S):	Ottenheijm, Harry C. J.; Liskamp, Rob M. J.; Van Nispen, Simon P. J. M.; Boots, Hans A.; Tijhuis, Marian W.
CORPORATE SOURCE:	Dep. Org. Chem., Univ. Nijmegen, Nijmegen, Neth.
SOURCE:	Journal of Organic Chemistry (1981), 46(16), 3273-83 CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE:	Journal
LANGUAGE:	English

GI



I



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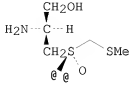

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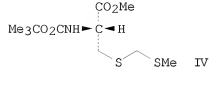
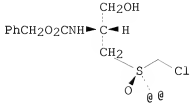
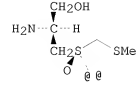


IV



V



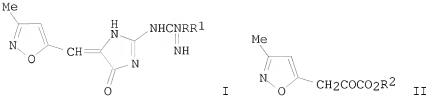
VI

AB The total syntheses of sparsomycin (I), a naturally occurring antibiotic and antitumor substance, and its three stereoisomers are described for the first time. In a convergent approach, the carboxylic acid II and the amine III were synthesized followed by amide formation. The acid II was prepared (23% yield) from 6-methyluracil by coupling of the 4-formyl derivative with Ph3P:CHCO2Et. The synthesis of III was accomplished by the reaction of a cysteine α-halosulfoxide derivative with MeSNa. Alternatively, oxidation of the dithio acetals, e.g. IV, was unsatisfactory, yielding predominantly the undesired regioisomers. Procedures are given for the preparation and separation of the α-halosulfoxide diastereomers e.g. V. By use of these procedures, the amino alc. monoxodithioacetals III and VI were prepared in five steps (40% yield) from a D-cystine derivative having the SC chirality of sparsomycin. Finally, I and the SC diastereomer were prepared (40% yield) by mixed anhydride coupling of II with III and VI, resp. In addition, syntheses of the RC enantiomer and the corresponding diastereomer are described. The CD spectra of I and its three stereoisomers are also discussed.

L8 ANSWER 19 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1979:457006 CAPLUS
DOCUMENT NUMBER: 91:57006
ORIGINAL REFERENCE NO.: 91:9239a,9242a
TITLE: 2-Guanidino-4(5H)-imidazolone derivatives
INVENTOR(S): Honna, Ryuji; Ogawa, Kazuo; Toratani, Keiko; Hashimoto, Sadao; Suzue, Takashi
PATENT ASSIGNEE(S): Taiho Yakuhin Kogyo K. K., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 54019977	A	19790215	JP 1977-83207	19770711

JP 62024434 B 19870528
PRIORITY APPLN. INFO.: JP 1977-83207 A 19770711
GI



I II

AB The title derivs. I (R, R1 = H, H; Me, Me; Bu, H; PhCH2CH2, H) were prepared by reaction of II (R2 = alkyl) with H2NC(:NH)NHC(:NH)NRR1. Thus, a mixture of 3-methylisoxazole-5-carboxaldehyde 5.6, BzNHCH2CO2H 9, Ac2O 17.4, and NaOAc 4.1 g was stirred 0.5 h at 80-90° to give 55% α-benzoylamino-β-(3-methyl-5-isoxazolyl) acrylic acid, which was refluxed with HCl-saturated MeOH 2 h to give 70% II (R2 = Me; III). A mixture of 0.46 g Na and 3.36 g H2NC(:NH)NHC(:NH)NH2.H2SO4.2H2O in MeOH was kept 1 h at room temperature, refluxed 1 h, 3.66 g III added, and the whole refluxed 3 h to give 43% I (R = R1 = H; IV). Hypoglycemic and blood free fatty acid level lowering data of IV were given in rats.

L8 ANSWER 20 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1974:570560 CAPLUS
DOCUMENT NUMBER: 81:170560
ORIGINAL REFERENCE NO.: 81:26395a,26398a
TITLE: Resin for curing by exposing to ionizing radiation a mixture of a vinyl ester resin, an alkenyl aromatic monomer, and a 2-oxazoline or guanidine
INVENTOR(S): Mani, Inder
PATENT ASSIGNEE(S): Dow Chemical Co.
SOURCE: U.S., 3 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3810825	A	19740514	US 1971-143266	19710513
US 3882004	A	19750506	US 1973-391112	19730827

PRIORITY APPLN. INFO.: US 1971-143266 A3 19710513
AB Addition of .geq.0.3% N-containing curing accelerator to a thermosettable vinyl aromatic monomer-vinyl ester resin prepolymer mixture reduces the dosage of ionizing radiation needed for curing. The accelerators include 2-oxazolines, guanidines and alkylamines. Maleic anhydride [108-31-6] treated with 2-hydroxypropyl acrylate [999-61-1] gave the acid ester which was treated with 1,4-butanediol diglycidyl ether, mixed with styrene, and irradiated. The resin [53108-91-1] system required 2.8-3.0 Mrad dose of electron beam irradiation while the dose was 1.3-1.4 Mrad for a similar one containing 3% tetramethylguanidine [80-70-6].

L8 ANSWER 21 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1974:97478 CAPLUS
DOCUMENT NUMBER: 80:97478
ORIGINAL REFERENCE NO.: 80:15685a,15688a
TITLE: Unsaturated ester of polyhydroxy-bis-oxazolines
INVENTOR(S): Mileo, Jean C.; Sillion, Bernard

PATENT ASSIGNEE(S): Commissariat a l'Energie Atomique; Institut Francais du Petrole, des Carburants et Lubrifiants
SOURCE: Ger. Offen., 20 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2311387	A1	19730927	DE 1973-2311387	19730308
FR 2176192	A5	19731026	FR 1972-8730	19720313
BE 796433	A1	19730910	BE 1973-1004867	19730308
NL 7303459	A	19730917	NL 1973-3459	19730312
IT 981298	B	19741010	IT 1973-21455	19730312
JP 49000263	A	19740105	JP 1973-29368	19730313
GB 1385842	A	19750305	GB 1973-11925	19730313

PRIORITY APPLN. INFO.: FR 1972-8730 A 19720313

AB Polymethylenebis[(hydroxymethyl)oxazoline] acrylates were prepared and used in electron beam-curable coating compns. Thus, azelaic acid [123-99-9] was condensed with 2-amino-2-methyl-1,3-propanediol [115-69-5] to give heptamethylenebis[4-(hydroxymethyl)-4-methyloxazoline] [38836-05-4], which was esterified with acrylic acid [79-10-7] to give heptamethylenebis[4-(hydroxymethyl)-4-methyloxazoline] diacrylate (I) [50979-14-1]. A solution of 7 g I and 3 g styrene was coated on stainless steel and irradiated with a 500 kV electron beam in N, giving a cured thickness of 120 μ and average hardness 5H at a dose of 10 Mrad.

L8 ANSWER 22 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1973:5539 CAPLUS
DOCUMENT NUMBER: 78:5539
ORIGINAL REFERENCE NO.: 78:901a,904a
TITLE: Thermosetting acrylics containing oxazoline groups
INVENTOR(S): Dowbenko, Rostyslaw
PATENT ASSIGNEE(S): PPG Industries, Inc.
SOURCE: U.S., 6 pp. Division of U.S. 3,609,161 (CA 76;26516s).
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3692757	A	19720919	US 1970-89116	19701112

PRIORITY APPLN. INFO.: US 1970-89116 A 19701112

AB Unsatd., polymerizable oxazolines were prepared by dehydrating a hydroxyalkyl aminoethanol, and esterifying the alc. with a monocarboxylic acid, ester, or acid halide. The oxazolines were polymerized or copolymd. to form thermosetting films, useful as solvent-resistant protective coatings. Thus, a mixture of 68 parts AcOH and 105.1 parts 2-methyl-2-amino-1,3-propanediol was refluxed 4 hr at 158-203.deg. to form 168.4 parts 2,4-dimethyl-4-hydroxymethyl-2-oxazoline, which was treated with methacrylic acid in benzene to obtain 2,4-dimethyl-2-oxazoline-4-ylmethyl methacrylate (I) [35061-72-4]. I homopolymd. or copolymd. in xylene and BuOH with Me methacrylate, 2-hydroxyethyl methacrylate, acrylic acid, and 2-ethylhexyl acrylate in the presence of azobisisobutyronitrile to yield flexible, xylene-resistant coating compns.

L8 ANSWER 23 OF 25 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1959:111733 CAPLUS

DOCUMENT NUMBER: 53:111733
ORIGINAL REFERENCE NO.: 53:20021e-i,20022a-i,20023a-i,20024a-i,20025a-i
TITLE: Griseofulvin. XVII. Synthesis of 7-chloro-4,6-dimethoxy-2'-methylgrisan-3,4'-dione
AUTHOR(S): MacMillan, J.
CORPORATE SOURCE: Imp. Chem. Inds. Ltd., Welwyn, UK
SOURCE: Journal of the Chemical Society (1959) 2211-23
CODEN: JCSOA9; ISSN: 0368-1769
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

AB The synthesis is described of grisan and 3-coumaranone spirocyclopentane analogs of some griseofulvin (I) derivs. and of racemates of some I degradation products. (All m.ps. are corrected; absorption spectra determined in EtOH.) Et 6-hydroxy-3-methylcoumarone-2-carboxylate (II), m. 179° (EtOH), ν 1700 cm.-1, λ 313, 282, 241, 210 mμ (log ε 4.30, 4.07, 3.90, 4.24), was prepared in 60% yield by the method of Hantszch [Ber. 19, 292(1886)]. Treatment of II with Me2SO4 gave 30% 6-methoxy-3-methylcoumarone-2-carboxylic acid (III), m. 184°, and 25% III Et ester (IV), m. 74-5°, ν 1700 cm.-1, λ 312, 285, 243 mμ (log ε 4.44, 4.13, 3.97); esterification of III gave IV. 6-Methoxy-3-methylcoumarone-2-acetic acid (V) chloride and AcCH(MgOEt)CO2Et (VI) gave Et α-acetyl-β-oxo-6-methoxy-3-methylcoumarone-2-γ-butyrate (VII), oil, ν 1714, 1623, and 1587 cm.-1; Cu derivative (VIII), m. 175° (MeOH), ν 1715, 1692, 1671, 1587 cm.-1 VII (7 g.) and 15 ml. concentrated H2SO4 kept 3 days at -5°, diluted with 50 ml. H2O, extracted with Et2O, the Et2O solution extracted with aqueous NaHCO3, and the alkaline extract acidified gave 200 mg. V, m. 139-40°; recovery from the Et2O solution gave a pale yellow oil (IX). IX in EtOH passed through a C column, the resulting material triturated for a long time under petr. ether (X) at - 50°, and the solid further recrystd. at room temperature gave 2.8 g. Et 6-methoxy-3-methylenecoumaran-2-spiro-1'-(2'-methyl-4'-oxocyclopent-2'-en-3'-carboxylate) (XI), m. 122°, ν 1745, 1707, 1649, 1615, 1595 cm.-1, λ 327, 263, 231, 214 mμ (log ε 3.98, 4.12, 4.35, 4.31); 2,4-dinitrophenylhydrazone, m. 175-6° (C6H6-X). Cyclization of VIII with H2SO4 gave 45% XI. XI (150 mg.) hydrogenated at room temperature and pressure with a catalyst prepared in situ from 7 mg. PdCl2 and 75 mg. C in 10 ml. AcOH (1 mole H absorbed), the recovered gum chromatographed in Et2O on Al2O3, eluted with Et2O, and the product repeatedly triturated with X at 0° gave 105 mg. corresponding 3-Me analog, m. 77-8°, ν 1738, 1698, 1610 cm.-1, λ 320, 302, 281, .apprx.263,228 mμ (log ε 2.78, 3.45, 3.59, 3.72, 4.25); 2,4-dinitrophenylhydrazone, m. 160° (C6H6-petr. ether). A stream of O3-O passed into 500 mg. XI in 30 ml. CCl4 until the solution became opaque, the filtered solution evaporated, the residual gum mixed with 25 ml. H2O, kept 24 hrs., and the aqueous phase distilled into saturated dimedon (XII) solution in 10% aqueous alc. gave XII derivative of CH2O, m. 191-2°; an Et2O solution of the residual gum chromatographed on Al2O3, the lowest bright-blue fluorescent band eluted with Et2O and the recovered product boiled with X (110 mg. solid obtained); the solid combined with 100 mg. slightly impure material from the following band fluorescing greenish-blue and recrystd. (petr. ether) gave 200 mg. corresponding 3-oxo compound (XIII), m. 115-17°, ν 1751, 1715, and 1701 cm.-1, λ 321, 275, 232 mμ (log ε 3.98, 4.21, 4.23); mono-2,4-dinitrophenylhydrazone, m. 243° (decomposition) (C6H6-petr. ether). Oxidation of 100 mg. XIII with Fehling's solution gave 25 mg. 2,4-HO(MeO)C6H3CO2H, m. 154-5°. XIII (70 mg.) and 17.5 ml. 2N HCl and 14 ml. EtOH refluxed 6 hrs. under N cooled (15 mg. solid separated), EtOH removed in vacuo (15 mg. solid and 30

mg. XIII separated), the combined product purified through the Na salt, and recrystd. (EtOH) gave 23 mg. corresponding acid (XIV), m. 175-7°, ν 1716 and 1697 cm.-1, λ 318, 273, 232, 210 mμ (log ε 4.05, 4.25, 4.30, 4.45). XIV (70 mg.) heated 10 min. at 190-200° in an N atmospheric, the residue sublimed in situ in vacuo, and the sublimate recrystd. (aqueous Me2CO) gave 40 mg. 6-methoxy-3-oxocoumaran-2-spiro-1'-(2'-methylcyclopent-2'-en-4'-one) (XV), m. 193-5°, ν 1713 cm.-1, λ 320, 273, 232, 209 mμ (log ε 3.92, 4.07, 4.16, 4.40); mono-2,4-dinitrophenylhydrazone, m. 238-40° (EtOAc). XV (15 mg.) in 1.5 ml. EtOAc added to a previously catalyst prepared from 10 mg. PdCl2 and 40 mg. C in 1 ml H2O, the mixture shaken with H at room temperature and pressure until absorption ceased (2.4 moles H absorbed in 5 min.), and the product (XVI) (13 mg.) recovered; XVI (13 mg.) chromatographed in C6H6 on Al2O3, a bright-blue fluorescent band eluted with C6H6, the product (2 mg.) recovered, sublimed, and crystallized (petr. ether) gave 0.8 mg. 6-methoxy-3-oxocoumaran-2-spiro-1'-(2'-methylcyclopentane), m. 167-8°, identical with the product from condensation of 6-methoxycoumaran-3-one and CH2Br(CH2)2CHBrMe (cf. preceding abstract).

β-Propiolactone (XVII) (8.64 g.) and 19.44 g. 6-methoxy-3-methylcoumarone refluxed 6 hrs. at 200°, the cooled residue ground with aqueous Na2CO3, the mixture filtered, the Et2O-washed filtrate acidified, the precipitate filtered off, sublimed in vacuo, and the sublimate crystallized (dilute EtOH) gave 4.9 g. 6-methoxy-3-methyl-coumarone-2-β-propionic acid (XVIII), m. 137°, ν 1707 cm.-1, λ 292 and 253 mμ (log ε 3.80, 4.16). 6-Methoxy-3-methylcoumarone-2-acetic acid (440 mg.) and 1 ml. SOCl2 was warmed gently until a clear solution was obtained, volatiles removed in vacuo below 30°, the residual oil in 10 ml. Et2O added at 0° to a 3-fold excess CH2N2 in 15 ml. Et2O, the solution kept 24 hrs. at 0°, and the Et2O removed in vacuo; the residual crude diazo ketone (m. 118-23°) in 10 ml. dioxane added dropwise with stirring to 2 g. Ag2O in 1 g. Na2S2O3 and 1 g. K2CO3 in 20 ml. H2O at 50-60° (N evolved), after 20 min. the mixture heated 10 min. at 70° and 5 min. at 90°, filtered, the filtrate acidified with dilute HNO3, the oil triturated with H2O, the resulting semisolid sublimed in vacuo, and the sublimate crystallized (dilute EtOH) gave 60 mg. XVIII, m. 137-8°. XVIII treated with PCl5 gave the acid chloride (XIX), green oil; amide, plates (C6H6-petr. ether). XIX in 500 ml. Et2O mixed with a suspension of VI [from 2.7 g. AcCH2CO2Et (XX), 1.2 ml. EtOH, and 0.48 g. Mg in 50 ml. Et2O], the mixture refluxed 24 hrs., excess dilute AcOH added, the separated Et2O layer washed with aqueous NaHCO3 (from the alkaline wash 200 mg. XVIII was isolated on acidification), concentrated, the oil (4.2 g.) chromatographed in C6H6 on Al2O3 and eluted with C6H6 gave, from a narrow fluorescent band, 90 mg. oil, which, on crystallization (petr. ether), afforded 60 mg. XVIII Et ester (XXI), m. 51-2°, ν 1737, 1624, 1594 cm.-1, identical with material obtained by esterifying XVIII, and, from a greenish-red band, 3.1 g. oil, which, heated 4 hrs. at 100-10°/10-4 mm., yield 2.2 g. crude oxo ester (XXII), giving an intense Fe+++ reaction in EtOH and forming a Cu chelate. Crude XXII (12 g.) in 25 ml. concentrated H2SO4 kept 8 days at 0°, worked up as described above for the lower homolog, and the alkaline extract acidified gave a yellow precipitate which decomposed on filtration; the unfiltered mixture extracted with C6H6, the extract passed through silica, and eluted with C6H6 gave 600 mg. XVIII, m. 133-5°; the Et2O solution concentrated, the oil (4.5 g.) chromatographed in Et2O on Al2O3, and eluted with Et2O gave, from a narrow band, 20 mg. XXI, and, from a pale blue band, 4.1 g. oil, which, crystallized (EtOH) and recrystd. (aqueous EtOH), afforded 3.8 g. Et 6-methoxy-2'-methyl-3-methylene-4'-oxogris-2'-ene-3'-carboxylate (XXIII), m. 97-8°, ν 1728, 1668, 1641, 1614 cm.-1, λ 326, 316,

273, 260, 233, 215 mμ (log ε 4.05, 4.09, 4.18, 4.43, 4.37); 2,4-dinitrophenylhydrazone, m. 182° (decomposition). Crude XXII (1.5 g.) mixed with 20 g. polyphosphoric acid (XXIV), kept 4 days at room temperature, and worked up gave 700 mg. XXIII, 30 mg. XXI, and no acidic product. XXIII (1.0 g.) in 30 ml. CCl4 ozonized as above (CH2O isolated with XII), the product chromatographed in Et2O on Al2O3, the yellow gum (510 mg.) treated with EtOH, seeded, and the solid recrystd. (dilute EtOH) gave Et 6-methoxy-2'-methyl-3,4'-dioxogris-2'-ene-3'-carboxylate (XXV), m. 110–11°, ν 1735, 1704, 1686 cm.-1, λ 320, 272, 231, 208 mμ (log ε 3.95, 4.12, 4.17, 4.42), giving an intractable precipitate with Brady reagent. XXV (3 g.) refluxed 4 hrs. in an N atmospheric with 300 ml.

EtOH and 350 ml. 2N HCl (0.6 mole CO2 evolved), the solution concentrated in vacuo, the aqueous residue extracted with Et2O, the extract washed with aqueous NaHCO3 (recovery gave only a trace of acidic gum), concentrated, the residual oil (1.6 g.) chromatographed in Et2O on Al2O3, and eluted with Et2O gave, from a blue band, 1.5 g. 6-methoxy-2'-methylgris-2'-ene-3,4'-dione, gum, ν 1713 and 1667 cm.-1, λ, 318, 272, 232, 209 mμ (log ε 3.98, 4.13, 4.22, 4.45) [2,4-dinitrophenylhydrazone, m. 230° (EtOAc)], and, from a dark blue band, 20 mg. XXV. 3,2,4,6-Cl(HO)(MeO)2C6HAc (XXVa) (46.0 g.), 66.4 g. CH2BrCO2Et, and 56.0 g. anhydrous K2CO3 in 700 ml. Me2CO refluxed 72 hrs., filtered, the filtrate evaporated in vacuo, the oil dissolved in 200 ml. EtOH, the solution treated with Et2O, and the precipitate recrystd. (EtOH) gave 56.6 g. 2,6,3,5-Ac(Cl)-(MeO)2C6HOCH2CO2Et (XXVI), m. 72°, ν 1763, 1735, 1684 cm.-1, λ 305, 292, 258, 223 mμ (log ε 3.35, 3.43, 3.70, 4.21); 2,4-dinitrophenylhydrazone m. 136° (EtOAc). With CH2-BrCO2Me in the above experiment, there was obtained the corresponding Me ester (XXVII), m. 103–4° (MeOH), ν 1760 and 1680 cm.-1, λ 305, 293, 268, 233 mμ (log ε 3.35, 3.42, 3.66, 4.20). XXVI (47.4 g.) in 200 ml. EtOH, 300 ml. H2O, and 14 ml. H2SO4 refluxed 4 hrs., diluted with H2O until cloudy, kept overnight at 5%, the precipitate filtered off, washed with aqueous Na2CO3 (19.7 g. XXVI remained), and the alkaline extract acidified gave 19.1 g. acid (XXVIII), m. 144° (C5H6 or H2O), ν 1751 and 1659 cm.-1, λ 301, 292, 258, 224 mμ (log ε 3.42, 3.39, 3.66, 4.19). XXVII (500 mg.) and 20 ml. 3N HCl refluxed 6.5 hrs., the solid filtered off, dissolved in warm aqueous Na2CO3, the solution treated with C, filtered, and the filtrate acidified at 0° gave 311 mg. XXVIII cyclic form (XXIX) (R = H) (XXX), m. 143–4° (dilute EtOH), ν 1746 cm.-1, λ 275 and 240 mμ (log ε 3.09, 3.95); mixts. of XXVIII and XXX m. 115–40°; a 1:1 mixture (XXXI), m. 119–20°, behaved as a pure compound (see below). XXVII (1.5 g.) and 75 ml. N HCl refluxed 4 hrs. and worked up gave 1.1 g. XXX, m. 119–20° (C6H6), ν 1749 and 1659 cm.-1, identical with a 1:1 mixture XXVIII and XXX. XXX (29 mg.) in 5 ml. Et2O treated overnight with 1 mole CH2N2 in 5 ml. Et2O and worked up gave 24 mg. XXIX (R = Me) (XXXII), m. 97° (MeOH), ν 1742 cm.-1, λ .apprx.275 and 235 mμ (log ε 3.07, 3.98). XXVIII treated similarly gave the isomeric open-chain acid (XXXIII), m. 103–4°, mixed m.p. with XXXII 78–85°. XXXIII or XXXII (17.3 g.), 34 g. fused NaOAc, and 100 ml. Ac2O heated under reflux until CO2 evolution ceased (30 min.), the cooled solution diluted with H2O, made alkaline with Na2CO3, the product filtered off, passed through a column of Al2O3 in 3 l. C6H6 recovered, and crystallized (EtOH) gave 14 g. 7-chloro-4,6-dimethoxy-3-methylcoumarone (XXXIV), m. 148°, ν 1626, 1611, 1591 cm.-1, λ 320, .apprx.275, 263, 220, 216 mμ (log ε 2.42, 4.00, 4.19, 4.56, 4.56). XXVI (15.8 g.) refluxed 1 hr. with 1 g. Na in 50 ml. EtOH, the cooled solution diluted with 750 ml. H2O, the precipitate (2.7 g.) filtered off, and crystallized (EtOH) gave Et 7-chloro-4,6-dimethoxy-3-methylcoumarone-2-carboxylate (XXXV), m. 172–3°, ν 1712 cm.-1, λ 312, 298, 245, 230 mμ (log ε 4.32, 4.37, 4.34, 4.30); acidification of the filtrate with dilute

HCl gave 11.2 g. XXVIII, m. 143°. XXXV (895 mg.) warmed 10 min. at 40° with 6 g. NaOH in 100 ml. 50% aqueous EtOH, diluted with ice and H_2O, the solution acidified, and the precipitate (790 mg.) sublimed in vacuo gave the corresponding acid (XXXVI), m. 310° (decomposition), ν, 1671 cm.$^{-1}$, λ 293 and 238 mμ (log ε 4.26, 4.31); Me ester, m. 196° (MeOH). XXXVI converted to the acid chloride ($SOCl_2$ plus C_5H_5N) and the latter treated with CH_2N_2-Et$_2O$ gave the diazo ketone (XXXVII), m. 118-20° (Et$_2O$). Attempted Wolff rearrangement of 600 mg. XXXVII as above gave 530 mg. XXXVI, m. 250-60° (decomposition). XXXVI (200 mg.) in 0.5 ml. quinoline heated 5 min. at 190-5° with 100 mg. Cu bronze and worked up gave 150 mg. XXXIV, m. 143°. Anhydrous HCN (200 ml.) added to 142 g. XXXIV in 6 l. Et$_2O$ at 0°, a fast stream of dry HCl passed in at 0-5° until absorption ceased (6 hrs.), the solution kept overnight at 0°, the aldimine-HCl (XXXVIII) filtered off, washed with Et$_2O$, heated with 10 l. H_2O at 100%, and the product (XXXIX) (110 g.) filtered off (after 24 hrs. a 2nd crop XXXVIII separated from the Et$_2O$ mother liquor which yielded 27 g. addnl. XXXIX on hydrolysis); XXXIX in C_6H_6 passed through Al_2O_3, crystallized (C_6H_6, EtOH, or Me_2CO), sublimed, and the sublimate recrystd. (Me_2CO) gave the 2-OHC derivative (XL) m. 183°, μ 1662 cm.$^{-1}$, λ 341, 312, 253 mμ (log ε 4.24, 4.16, 4.28) [2,4-dinitrophenylhydrazone m. 312°(Me_2CO); azlactone m. 235°(EtOAc), giving on alkaline hydrolysis 7-chloro-4,6-dimethoxy-2,3-dimethylcoumarone (XLI), m. 290° (MOH), μ and 1596 cm.$^{-1}$]. XL oxidized with KMnO_4 in aqueous Me_2CO gave XXXVI, m. 310° (decomposition). XL (2.26 g.) and 720 mg. XVII refluxed 4 hrs., cooled, the melt dissolved in 200 ml. Et$_2O$, the solution filtered, the filtrate extracted with aqueous Na_2CO_3, and the alkaline extract acidified gave 720 mg. 7-chloro-4,6-dimethoxy-3-methylcoumarone-2-β-propionic acid (XLII), m. 123-30° (chromatography followed by recovery from the Ag salt); a sample of XLII was converted by Et$_2O$-CH_2N_2 to the Me ester (XLIII), m. 102° (MeOH), ν 1739 cm.$^{-1}$, λ 320, 294, 278, 265, 226, 223 mμ (log ε 2.61, 3.30, 4.05, 4.27, 4.53, 4.52, 4.52). The remaining XLII (500 mg.) methylated as above, the product chromatographed in C_6H_6 on Al_2O_3, a pale-blue band eluted with Et$_2O$, the recovered ester (350 mg.) hydrolyzed with N alc. HCl, the compound sublimed in vacuo, and recrystd. (aqueous EtOH) gave XLII, m. 134-5°, ν (Nujol mull) 1722 and 1706 cm.$^{-1}$, (in $CHCl_3$) 1716 cm.$^{-1}$ XXXIX (4 g.), 6.7 g. $CH_2(CO_2H)_2$, 330 mg. piperidine, and 17 ml. C_5H_5N heated 1 hr. at 100° and then 10 min. at 120°, the cooled solution acidified, the precipitate (6.1 g.) extracted with aqueous Na_2CO_3 (1.3 g. XXXIV remained), and the alkaline extract acidified gave 4.75 g. 7-chloro-4,6-dimethoxy-3-methylcoumarone-2-acrylic acid (XLIV), m. 252° (C_6H_6), ν 1692 and 1676 cm.$^{-1}$, λ 329 and 255 mν (log ε 4.44, 4.04); Me ester, m. 179° (MeOH), ν 1709 cm.$^{-1}$ (a) XLIV (102 mg.) in 50 ml. AcOH added to 0.2 g. Raney Ni in 2 ml. EtOH, hydrogenated at room temperature and pressure until absorption ceased (1 mole H absorbed in 8 hrs.), the mixture filtered, the filtrate concentrated to 5 ml. in vacuo, 100 ml. H_2O added, stored overnight at 5°, the solid (60 mg.) collected, stirred 1 hr. with cold dilute HCl, the mixture filtered, the precipitate (35 mg.) purified through the Na salt, and crystallized (petr. ether) gave XLII, identical with XLII as prepared above. (b) Crude XLIV (93 g.) in 3.5 l. 0.1N NaOH hydrogenated at room temperature and pressure in the presence of 50 g. 5% Pd-$SrCO_3$ (absorption ceased after 8 hrs. when 0.64 mole H was absorbed), 10 g. C added, the filtered solution acidified (38 g. solid obtained and an addnl. 5 g. by repptg. the sticky material from aqueous NaOH), and the product chromatographed in C_6H_6 on silica gave 39 g. XLII, m. 133-5°, identical with XLII prepared in a. (c) XLIV (56 g., m. 252°) in 2.3 l. 0.1N NaOH hydrogenated as in b (2 moles H absorbed in 1 hr.), the acidified solution extracted with Et$_2O$, the exts.

concentrated, the combined solids therefrom treated with CH_2N_2-Et_2O, the resulting oil (50.7 g.) chromatographed in C_6H_6 on Al_2O_3, and a single bright blue band eluted with C_6H_6 gave 6.3 g. product (XLV), needles, m. 104-6° (C_6H_6-petr. ether), and 3.6 g. product (XLVI), prisms, m. 98-100° (MeOH), and, on further elution, 37 g. gum (XLVII). XLV crystallized (MeOH) gave Me 7-chloro-4,6-dimethoxy-3-methylcoumaran-2-β-propionate, prisms, m. 107-8°, ν 1731 cm.-1, hydrolyzed with boiling N NaOH to the corresponding acid, m. 147-8°, ν 1716 cm.-1 XLVI recrystd. (MeOH) gave 2.7 g. XLIII, m. 102°, alkaline hydrolysis giving 1.9 g. XLII. XLVII rechromatographed, the single band eluted in 10 equal fractions with C_6H_6, and fractions 2 and 8 rechromatographed; fraction 2 gave essentially Me 4,6-dimethoxy-3-methylcoumaran-2-β-propionate (XLVIII), uncrystallizable gum, ν 1728 cm.-1, alkaline hydrolysis yielding the acid (XLIX), m. 114° (1:1 Et_2O-petr. ether); fraction 8 hydrolyzed with NaOH, the product crystallized (1:1 C_6H_6-petr. ether), the crystals hand-picked, and recrystd. gave 4,6-dimethoxy-3-methylcoumarone-2-β-propionic acid (L), m. 124°. XLIX (2 g.) and 200 mg. S heated 20 min. at 220° and 5 min. at 280°, the product continuously extracted with X, and the resulting crystallized extract hand-picked gave 320 mg.
recovered XLIX and 540 mg. L, m. 124°. XLVIII (157 mg.) and 135 mg. o-chloranil in 5 ml. $CHCl_3$ stored 1.5 hrs. in the dark, the recovered product chromatographed in C_6H_6 on Al_2O_3, the pale blue band eluted with C_6H_6, and the product (135 mg.) crystallized (1:1 Et_2O-petr. ether and then MeOH) gave the coumarone-tetrachloropyrocatechol complex (LI), m. 117°. LI hydrolyzed by alkali and the product crystallized (1:1 Et_2OX) gave L, m. 122-4°. XLII (23.5 g.) in 500 ml. dry $CHCl_3$ treated with 20 g. PCl_5, the mixture refluxed 0.5 hr., volatile products removed at 30° in vacuo, and the residue (LII) kept 4 hrs. at 12 mm., LII dissolved in 1.5 l. Et_2O, 12 g. VI added, the mixture refluxed 24 hrs., 250 ml. 40% AcOH added, the Et_2O layer separated, extracted with Na_2CO_3 solution (the extract afforded 5.9 g. XLII), and concentrated; the residual oil (25 g.) chromatographed in Et_2O on Al_2O_3 and eluted gave, from a bright-blue band, 800 mg. XLII Et ester (LIII), m. 74-6° (EtOH), and, from an orange-red band, 18 g. orange oil (LIV).

LIV heated 2 hrs. at 110°/10-4 mm. (excess XX removed) gave 14 g. gum (LV), giving a red color with alc. $FeCl_3$ and forming no stable ketonic derivs. LV (12 g.) in 100 ml. Et_2O shaken with saturated aqueous $Cu(OAc)_2$ deposited 2.8 g. blue crystals (LVI); the Et_2O layer evaporated and the residual gum fractionally crystallized gave 6 g. product (LVII) and 1.8 g. Et α-acetyl-β-oxo-7-chloro-4,6-dimethoxy-3-methylcoumarone-2-γ-carboxylate (LVIII) β-Cu chelate (LIX), m. 98-100° (EtOH), converted to the α-Cu isomer (LX) on continued heating at 120-30°; LVI and LVII combined and crystallized ($CHCl_3$) gave LX, m. 164°. (a) LIX (1.4 g.) and 20 g. XXIV kept 10 days at room temperature, diluted with 50 ml. ice and H_2O, extracted with Et_2O, the extract washed with aqueous Na_2CO_3, dried, evaporated, the residual gum (1.18 g.) chromatographed in C_6H_6 on Al_2O_3, and the column eluted with C_6H_6 gave (1) from a narrow blue band, 5 mg. LIII, m. 72-3°, (2) from a greenish-blue band, a gum, which, kept in EtOH, deposited 175 mg. product (LXI), m. 137° and (3) from a blue band, a gum, which, kept in X, deposited 278 mg. product (LXII), m. 129-31°. LXI and LXII combined, recrystd. (EtOH), the crystals (410 mg.) sublimed in vacuo, and the sublimate recrystd. (MeOH) gave Et 7-chloro-4,6-dimethoxy-2'-methyl-3-methylene-4'-oxogris-2'-ene-3'-carboxylate (LXIII), m. 137°, ν 1731, 1680, 1638, 1610 cm.-1, λ282, .apprx.275, and 253 mμ (log ε 4.30, 4.28, 4.57). (b) LX (500 mg.) and 20 g. XXIV heated 1 hr. at 70-80° and worked up as above gave 210 mg. LXIII, m. 137°. (c) LX (1.8 g.) and 30 g. XXIV kept 10 days at room temperature, worked up as above, and the alkaline extract

acidified gave 600 mg. XLII; some Cu derivative (600 mg.) was regenerated by shaking the acid with aqueous Cu(OAc)2; the remaining gum (320 mg.) chromatographed gave 120 mg. LIII and 5 mg. unidentified compound, m. 181-2°. (MeOH). LXIII (248 mg.) in 15 ml. CCl4 ozonized 8 min. at room temperature, CCl4 removed in vacuo, the residue in 20 ml. Et2O and 10 ml. AcOH cooled in ice, treated with 2 ml. H2O and 100 mg. Zn dust, after 12 hrs. 20 ml. H2O added, the Et2O layer separated, combined with Et2O-washings of the aqueous layer, and worked up gave 5% LXIII, 40% XXVa, 30% Cl-free acidic fraction, and 4% 7-chloro-4,6-dimethoxy-2'-methylgris-2'-ene-3,4'-dione (LXIV), m. 167-8°, ν 1718 and 1683 cm.-1, λ 323, 291, 235, 213 mμ (log ε 3.70, 4.30, 4.19, 4.42). LXIII (137 mg.) in CCl4 ozonized 0.5 hr. and worked up gave 10 mg. Cl-free solid, 30 mg. XXVa, 6 mg. LXIII, 1.2 mg. unidentified product, m. 143-9°, and 13 mg. Et 7-chloro-4,6-dimethoxy-3,4'-dioxogris-2'-ene-3'-carboxylate, m. 174° (EtOH), ν 1739, 1705, 1684, 1623, 1593 cm.-1, not hydrolyzed by boiling 1-10N HCl, alkaline hydrolysis causing degradation. LXIV (10 mg.) in 1 ml. EtOAc added to a previously reduced catalyst prepared from 5 mg. PdCl2 and 20 mg. C in 1 ml. H2O, shaken 6 hrs. with H at room temperature and pressure (absorption complete in 3 hrs.), the recovered gum chromatographed in C6H6 on Al2O3, and the recovered gums from each eluate chromatographed on circular paper gave an alc. fraction (not investigated) and the racemate of 1,d-7-chloro-4,6-dimethoxy-2'-methylgrisan-3-one, d,d-7-chloro-4,6-dimethoxy-2'-methylgrisan-3,4'-dione, m. 170-5°.

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TITLE:	Transesterification of methyl methacrylate with amino alcohols. Preparation of a primary aminoalkyl methacrylate and 2-isopropenyl-4,4-dimethyloxazoline
AUTHOR(S):	De Benneville, Peter L.; Luskin, Leo S.; Sims, Homer J.
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GI For diagram(s), see printed CA Issue.

AB (All nD and d. at 25°). Me2C(NH2)(CH2)3CHMe(CH2)2CH2OH (57.6 g.), 66.6 g. CH2:CMeCO2Me (I), 2 g. Al(OPr-iso)3, and 7.2 g. di-β-naphthol (II) heated 10 hrs. under a 20-cm. Vigreux column and total reflux distillation head (23 g. distillate collected, about half between 65-70°, and the remainder as the temperature slowly rose to 98°) and the product fractionated gave 74 g. (crude) CH2:CMeCO2(CH2)3CHMe(CH2)3C(NH2)Me2 (III), b0.8 115-20°, nD 1.4570, d. 0.9215, ν 1724, 1641, and 1565 cm.-1, giving a tacky polymer when heated 16 hrs. at 70° with 1% di-Me azoisobutyrate (IV). (Procedure A) Me2C(NH2)CH2OH (V) (89 g.), 220 g. I, and 10 g. II heated 1 hr. under a short column (to remove a small amount H2O), 1 g. Ti(OPr-iso)4 (VI) added, distillation continued 15 hrs. (more VI added after 4 and 11 hrs.), the pot temperature adjusted to keep the overhead temperature below 70° as long as possible, and the residue fractionated, the crude product fractions combined, treated with 25 g. EtNCO in 200 cc. pentane, and the 2 layers formed distilled twice gave 52.3 g. O.C(CMe: CH2):N.CMe2.CH2 (VII), b30 62-3°, from the upper layer, and from the lower layer 11 g. VII, b36, 65-6°, nD 1.4536-1.4540, d. 0.9181, neutralization equivalent 142. In a run of similar size, the pot temperature held below 110° by operation at 400 mm., the crude product (89.5 g., b34 59-62°) dried over Na, and distilled gave 60% VII, b. 149°, ν 1658 and 1613 cm.-1, λ (isooctane) 225 mμ (log ε 3.79) (inflection).

A slight excess of saturated aqueous Na picrate solution added to 1.39 g. VII in 20

ml. 0.5N NCl, the precipitate collected, and dried at 50° gave 2.6 g. VII picrate, m. 115-16°. (a) VII (28 g.) shaken 48 hrs. with PtO2 under 50 lb. H pressure, fresh PtO2 added, shaking continued 24 hrs., the mixture filtered, distilled in vacuo, the distillate (17.4 g., b29 50-2°) dried over Na, and redistd. gave O. C(Pr-iso):-N.CMe2.CH2 (VIII), b35 56°, nD 1.4218, d. 0.8797, ν 1665 cm.-1 and 1612 cm.-1 (b) V (89 g.) added to 89 g. Me2CHCO2H, the salt heated 5 hrs. under a distillation head (a 2-phase distillate formed), the wet product layer separated,
dried over Na, and distilled gave 93 g. VIII, b28 50-3°, nD 1.4210, d. 0.8770, ν 1665 cm.-1, ultraviolet end absorption below 245 mμ (Procedure B). V (1 mole) and 1 mole CH2:CMeCO2H treated as above gave 60 g. impure VII, b35 64-7°, nD 1.4492, neutralization equivalent 143. CH2:CMeCOCl (IX) (104.5 g.) added with stirring at 10-15° to 185 g. V in 100 ml. C6H6 during 2.5 hrs., the mixture stirred 3 hrs., refrigerated overnight, filtered, the solids washed with C6H6, the combined filtrates evaporated, and the residual oil (169 g.) distilled in the presence of p-HOC6H4NHPh gave 140 g. CH2:CMeCONHCMe2CH2OH (X), b0.15 97°, nD 1.4785, ν 1660 and 1621 cm.-1 (c) X (32 g.) heated 4 hrs. at 175-80° and the crude product separated gave 24.3 g. VII, nD 1.4545. In the presence of a few drops concentrated H2SO4, the distillation was completed in
1.5 hrs. at 180-90° and the product (24.5 g.) dried over Na, and redistd. gave 67% VII, identical with the material obtained by transesterification. Me2C(OH)CH2NH2 and IX treated as above, the solids dissolved in 100 ml. H2O, the solution extracted with two 50-ml. portions CHC13,
and the extract evaporated finally in vacuo gave 34.5 g. CH2:CMeCO2NHCH2C(OH)Me2,
m. 70-5°, nondistillable. VII (1 g.) containing 0.01 g. IV heated 24 hrs. at 75° gave a polymer, soluble in H2O and C6H6.

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AB OXAZOLE SECTION: New methods for constructing the oxazole ring have been devised and the behavior of functional groups elucidated. The synthesis of oxazoles and imidazoles from K β-hydroxy-α-(α-alkoxyalkylideneamino)acrylates is given. A mixture of 51.1 g. AmCN and 24.5 g. EtOH was kept with 19.2 g. dry HCl below 0° for 2 wk, decomposed with 74 g. K2 CO3 in Et2O and distilled The crude AmC(OEt):NH (62.4 g.), b11 52-65°, was shaken with cold aqueous H2NCH2CO2Et.HCl for 1 h. The upper layer was fractionated to yield Et α-ethoxycaprylideneaminoacetate (I),b0.5 91°, saponified on gentle warming to AmCO2Et. The corresponding Me α-methoxycaprylideneaminoacetate (Ia), b0.1 74°, was similarly prepared A solution of 0.85 g. K in 2.5 g. EtOH and 14 g. Et2O was diluted to 50 mL. with Et2O, cooled to -15° and treated with a similarly cooled mixture of 4.85 g. I and 3.2 g. HCO2Et, yielding after 3 h. at -10°, 2.6 g. of hygroscopic needles of C5H11C(OEt):NC(CO2Et):CHOK (II). The corresponding K Me β-hydroxy-α(α-methoxycaprylideneamino) acrylate (IIa) was obtained in 3.2 g.-yield from 3.75 g. Ia. Treatment of 2.6 g. II and 1.25

g. DL-penicillamine in 5 cc. EtOH with alc.-HCl gave crystalline DL-N-caproylpenicillamine, m. 137-8°. Treatment of II with ethereal HCl produced Et 2-amyl-oxazole-4-carboxylate, b0.07 99° (dinitrophenyl-hydrazone, m. 165-6°; amide, m. 152°) saponified to 2-amyl-oxazole-4-carboxylic acid, m. 92-3° (PhNH2 salt. m.98.5-9.5°) readily decarboxylated to 2-amyl-oxazole, b. 172-3°; picrate, m. 84.5-5.5°. This general synthesis of 2-substituted oxazoles and their 4-carboxylic acids has been extended to Et 2-phenyloxazole-4-carboxylate, m. 69-70°, the corresponding acid, m. 209°, and carried through to the known 2-phenyloxazole. The method can be also applied to the synthesis of imidazoles. Treatment of I with aqueous NH4OH gave 2-amylimidazole-4-carboxylic acid, m. 230° (decomposition); with MeNH2.HCl or alc. H2NCH2CO2Et.HCl, I produced, resp., Et 2-amyl-1-methylimidazole-4-carboxylate (III), m. 42-3°, and Et 2-amylimidazole-4-carboxylate-1-acetate (IIIa), m. 61°. Similarly, Ia gave Me 2-amyl-1-methylimidazole, m. 66.7°, and Me 2-amylimidazole-4-carboxylate-1-acetate, m. 107°. Hydrolysis of III and IIIa yielded 1-methyl-2-amylimidazole-4-carboxylic acid, m. 121-3°, and 2-amyl-4-carboxyimidazole-1-acetic acid, m. 132-4°. Starting from PhCH2CN, Et 2-benzylimidazole-4-carboxylate-1-acetate, m. 111-2°, was likewise prepared, converted by treating with MeOH into a Me Et ester. On heating with aqueous NH4OH and with PhNH2, 2-amyl-oxazole-4-carboxylic acid was converted into 2-amylimidazole, m. 33-4° and 1-phenyl-2-amylimidazole, m. 143-4°. Synthesis of oxazoles by rearrangement of oxazolones. The Na salt of 2-benzyl-4-hydroxymethylene-5-oxazolone (2.7 g.) in 50 mL. absolute MeOH was treated with 5 mL. absolute Et2O containing 0.38 g. HCl. The gummy product (2.28 g.) was taken up in 10 mL. absolute MeOH and heated for 30 min. with 6.2 mL. H2O containing 0.42 g. NaOH. The residue on evaporation was dissolved in 10 mL. of iced H2O, acidified with dilute HCl to pH 6.5 and extracted with Et2O, yielding 700 mg. 2-benzyloxazole-4-carboxylic acid, m. 158°. On heating at 220°, crude 2-phenyl-4-(α-hydroxyethylidene)-5-oxazolone rearranged to 2-phenyl-5-methyloxazole (IV), m. 184-5° (decomposition). Similarly, on heating to 230°, Na 4-hydroxymethylene-g-amyl-5-oxazolone rearranged to 2-amyl-oxazole-4-carboxylic acid. Evaporation of 2-(1-pentenyl)-4-(hydroxymethylene)-5-oxazolone in NaOH and fusion of the residue at 250° under reduced pressure yielded 2-pentenyl-oxazole-4-carboxylic acid, m. 145-7°. Incidental syntheses of oxazole derivs. The action of PhSO3Ag on Me thiobenzylpenaldate di-Et acetal produced colorless prisms of 2-benzyloxazole-4-carboxylic acid, m. 156-7° and the dehydration of Et α-benzylamino-acetoacetate gave Et 2-phenyl-5-methyloxazole-4-carboxylate, m. 51-2°, hydrolyzed to the acid, m. 180-1°, decarboxylated at 220° in the presence of a trace of CuO to IV. Thus a reaction known to succeed with α-acylamino ketones and carboxylic esters is extended to β-keto esters. The 2-substituted oxazoles and their 4-carboxylic acids and esters are feebly basic, readily oxidized by cold aqueous KMnO4 but stable to Br in CCl4. The ring opens on warming with 2,4-(O2N)2-C6H3NHNH2 in 2N HCl with a tendency to formation of glyoxal osazone derivs. Rosenmund reduction of 2-amyl-oxazole-4-carboxylic acid chloride produced 2-amyl-oxazole-4-carboxaldehyde, b8 108° (2,4-dinitrophenylhydrazone, m. 172-3°), converted by warming with D-penicillamine-HCl in AcOH to the thiazolidine, devoid of antibiotic properties. From the corresponding Et ester, 2-benzyl-4-carboxyoxazole hydrazide, m. 81-3° and benzylamide, m. 121-2° were prepared In attempts to synthesize the thiazolidine-oxazolone structure for penicillin, attention was directed to the preparation of 5-alkoxyoxazoles and many variations of the general method of dehydrating α-acylamino

esters with P2O5 were introduced. By the use of PCl5, P2O5, POCl3, SOCl2, and PhSO2Cl, the following new oxazoles were prepared (substituent given): 2-Ph, 5-MeO, b9 141°; 2-Ph, 5-PhCH2O, m. 56°; 2-PhCH2, 5-EtO, b15 152-4°; 2-PhCH2, 5-MeO, m.31-2°; 2-Am, 5-EtO, b0.8 82-5°; 2-Am, 5-MeO, b1.0 60-65°; 2-(1-C5H9), 5-EtO, b20 125-8° (C5H9 = pentenyl); 2-(1-C5H9), 5-MeO, b15 108-10°; 2-PhCH:CH, 5-EtO, m. 35°; 2-PhCH:CH, 5-Ph CH2O, picrate, m. 135° (decomposition); 2-Ph, 4-Me, 5-EtO, b10 151°; 2-Ph, 4-Me, 5-PhCH2O, picrate, m. 112-13°; 2-PhCH2, 4-Me, 5-EtO, b15 145-50°; 2-Am, 4-Me, 5-EtO, b3 92°; 2,4-Ph2, 5-EtO, m. 47-8°; 2-Ph, 4-PhCH2, 5-EtO, picrate, m. 105°; 2-Ph, 4-PhCH2, 5-PhCH2O, picrate, m. 117°; 2,4-(PhCH2)2, 5-EtO, b0.3 145-50°; 2-Am, 4-PhCH:CH, 5-EtO, m. 92°; 2-Ph, 4-CO2Et, 5-EtO, m. 75°; 2-Am, 4-CO2Et, 5-EtO, b0.1 122-5°; 2-(1-C5H9), 4-CO2Et, 5-EtO, b0.2 125°; 2-PhCH2, 4-CO2Et, 5-EtO, b0.1 165°. The possibility of converting an alkoxyoxazole to the corresponding oxazolone was realized by the catalytic hydrogenation of 2 g. of 2-phenyl-5-benzyloxyoxazole in 30 mL. dry dioxane in the presence of Pd-black to 2-phenyl-5-oxazolone, m. 91°. The converse reaction, transformation of an oxazolone to an alkoxyoxazole, has also been achieved. Methylation of 3 g. of 2-phenyl-4-carbethoxy-5-oxazolone with 500 mg. CH2N2 in 50 mL. Et2O yielded 2-phenyl-4-carbethoxy-5-methoxyoxazole, m. 72°. Similarly, methylation of 2-phenyl-4-carbomethoxy-2-oxazolin-5-one gave 2-phenyl-4-carbomethoxy-5-methoxyoxazole, m. 98°, identical with that prepared by the dehydration of BzNHCH(CO2Me)2 with PCl5 in CCl4. Attempts to obtain 5-alkoxyoxazole-4-carboxaldehydes covered a wide range. Formylation of BzNHCH2CO2Et and condensation with PhCH2NH2 in Et2O gave Et β-benzylamino-α-benzamidoacrylate, R'NHCH:C(CO2Et)NHCOR (V; R = Ph, R' = PhCH2), m. 108°, cyclized by PBr3, POCl3 or PCl5 to 2-phenyl-4-benzylaminomethylene-5-oxazolone (VI), m. 134-7; Ac derivative, m. 140°. In the same way, Et β-benzylamino-α-phenylacetamido acrylate (VIa) with PBr3 gave 2-benzyl-4-benzylaminomethylene-5-oxazolone (VIb). Dehydration of Et α-benzamido-β,β-diethoxypropionate with PCl5-POCl3 yielded 2-phenyl-4-(ethoxymethylene)5-oxazolone (VII). Distillation of benzyl α-benzamido-β,β-diethoxypropionate gave a mixture of products including benzyl α-benzamido-β-ethoxyacrylate, m. 108-10°; benzyl 2-phenyloxazole-4-carboxylate, m. 106-7°; and VII. Attempts were made to cyclize α-benzyl-β-methyl-DL-phenylpenicilloate, HN.CH(CO2R').CMe2.S.CHCH(NHCOR)CO2CH2Ph (VIII, R = Ph, R' = Me) (VIIIa), m. 130°; dibenzyl-DL-phenylpenicilloate (VIII, R = Ph, R' = PhCH2) (VIIIb), m. 107-8°; and DL-2-(carboxy-1-hexenoylaminomethyl)-5,5-dimethyl-4-carbometh-oxythiazolidine benzyl ester (VIII, R = 1-pentenyl, R' = Me). (VIIIc). The action of PCl5 on VIII and VIIIa gave definite evidence of formation of thiazolidinylalkoxyoxazoles and cyclization of VIIIb and chromatog. purification of the product gave benzyl 2-(2-phenyl-5-benzyloxy-4-oxazolyl)-5,5-dimethylthiazolidine-4-carboxylate, m. 120-5°, absorption band at 2850 A. This reduced in EtOAc using a Pd-BaSO4 catalyst with 2 mol H, corresponding to removal of 2 PhCH2 groups, yielded a product with no-antibiotic activity. The simpler thiazolidines were also investigated. The reaction of 3-methyl-2-(benzamidocarbethoxymethyl)-thiazolidine with PCl5 gave a Cl-containing product, converted by NaHCO3 to a probable sulfoxide. With PCl3, a product was obtained, which was converted by aqueous KOH to 2-phenyl-4-hydroxymethylene-5-oxazolone. β-Methylaminoethyl mercaptan-HI (from 15 g. of-2-methylthiazoline-MeI) in 20 mL. H2O was treated with 11 g. of crude Na salt of C,N-diformylglycine Et ester and neutralized with AcOH. After 15 h., NaHCO3 was added and the dried CHCl3 exts. (120 mL.) were concentrated to give 6.55 g. of crude product, converted by treatment with 65.5 mL. of 10% HCl in EtOH to 4.4 g. of

2-(aminocarbethoxymethyl)-3-methylthiazolidine-2HCl (IX), m. 169-70° (decomposition). IX (10.0 g.) in 36.1 mL. of 2N NaOH and 35 mL. EtOH was stirred with 6.6 g. PhCH2CS2Me for 45 h., yielding 6.2 g. of colorless prisms of 2-[(phenylthioacetamido)carbethoxymethyl]-3-methylthiazolidine (X), m. 100-100.5°. Addition of 5.0 g X in 20 mL. CHCl3 to 8.6 g. PhSO3Ag and 2.5 mL. pyridine in 70-mL. CHCl3 gave no identifiable organic products. The action of PhSO3Ag on Me α-phenylthioacetamido-β,β-diethoxypropionate yielded a product from which Me-benzylpenaldate and 2-benzyloxazole-4-carboxylic acid were isolated. By the PCl5 method it has been possible to prepare 4-(2-thiazolyl)-2-benzyl-5-ethoxyoxazole and 2-(p-nitrophenyl)-4-(5,5-dimethyl-4-carbomethoxy-2-thiazolinyl)-5-ethoxyoxazole. Attempts to introduce a CHO group into the 4-position of 2-phenyl-5-ethoxyoxazole (XI) using PhNMeCHO and POCl3 gave 2-phenyl-4-anilinomethylene-5-oxazoline. With AcNHBr, XI gave 2-phenyl-4-bromo-5-ethoxyoxazole, b0.8 128°. The oxidation of 2-phenyl-4-methyl-5-ethoxyoxazole with SeO2, CrO3 or CrO2Cl2 resulted only in far-reaching breakdown. Condensation of PhCH2CH2COCO2H with AcNH2 or AmCONH2 gave α-acetamido- and α-caproyl-amino-γ-phenylisocrotonic acid (XII). Treatment of the Et ester of XII with PCl5 afforded 2-amyl-4-styryl-5-ethoxyoxazole (XIII), disrupted by ozonization with production of BzOH and H2NCOCO2Et. XIII (5.7 g.) in 100 mL. glacial AcOH was stirred with 9.0 g. of Pb(OAc)4 for 3 h., yielding 6.1 g. of 2-(1-acetoxyamyl)-4-styryl-5-ethoxyoxazole, m. 90-1°, degraded by distillation with loss of AcOH to 2-(1-pentenyl)-4-styryl-5-ethoxyoxazole (XIV), m. 100°, reduced catalytically to XIII. Oxidation of 2.83 g. XIV in 30 mL. tert-BuOH containing 0.75 g. H2O2 and 30 mg. OsO4 at 40-50° for 2 h. produced PrCHO and 5-ethoxy-4-styryl-oxazole-2-carboxaldehyde, m.130.5°, converted into the thiazolidine, m. 169°, using DL-penicillamine. Cyclization of AmCONHCH(CO2Et)2 in dry alc. free CHCl3 with PCl5, yielded 2-amyl-5-ethoxyoxazole-4-carboxylic acid (XIV), m. 63.4°, which on refluxing with PCl5 in CHCl3 gave Et 2-amyl-5-chlorooxazole-4-carboxylate (XV), b0.3 106°, catalytically reduced over Pd-BaSO4 in xylene to 2-amyl-oxazole-4-carboxylate, acidified to the free acid (XVa), m. 93-4°, converted by alc. EtONa to XIV. Treatment of 2 g. XVa with 1.09 g. PCl5 in 10 mL. CHCl3 and distillation produced the corresponding acid chloride, b0.3 96°, converted by (NH4)2CO3 in aqueous NH4OH to the amide, m. 90°, which, distilled with P2O5, gave 2-amyl-5-chloro-4-cyanooxazole (XVb), b0.15 72°. Reduction of 3.0 g. XVb in a suspension of 5.7 g. anhydrous SnCl2 in 40 mL. dry ether yielded unstable 2-amyl-5-chloro-oxazole-4-carboxaldehyde (XVI) (dinitrophenylhydrazone, m. 109-10°), rearranging in 3 days at room temperature or on low pressure distillation to 2-amyl-oxazole-4-carboxylic acid chloride. Despite its instability, XVI readily combined with D-penicillamine-HCl to produce D-2-(2-amyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carbo-xylic acid-HCl, m. 150-2° (decomposition). A similar series of compds. starting with Et 2-phenyl-5-ethoxyoxazole-4-carboxylate (XVII) and proceeding to the thiazolidine was later prepared XVII was saponified to the crystalline acid (XVIIa), m. 148°, converted to the acid chloride (XVIIb), m. 105-6°, and to Et 2-phenyl-5-chlorooxazole-4-carboxylate, m. 68°, by refluxing in xylene for 1 h. The corresponding acid (XVIII), m. 178-4° (decomposition), was converted through the acid chloride, m. 118-20°, the amide, m. 183°, and the cyano compound, m. 112°, to 2-phenyl-5-chlorooxazole-4-carboxaldehyde (XIX), m. 91-3°. The addition of 1.14 g. aldehyde in 5 mL. EtOH and 10 mL. Et2O to 0.93 g. D-penicillamine-HCl in 5 mL. H2O and 0.65 g. AcONa, and passage of HCl through a filtered ethereal solution of the reaction product, yielded 1.5 g. of 2-(2-phenyl-5-chloro-4-oxazolyl)-5,5-di-methylthiazolidine-4-carboxylic acid-HCl, m. 178° (decomposition); Me ester-HCl, m. 120-2°; free acid, m. 166°; Me ester, m. 154°; PhCH2 ester, m. 116-7°. The thiazolidine exhibited a

low order of antibiotic activity. A similar series of 2-benzyloxazole derivs. have been prepared but the corresponding thiazolidine was inactive: 2-benzyl-5-ethoxy-oxazole-4-carboxylic acid, m. 118° (decomposition); Et ester, b0.1 165°; acid chloride, m. 81-2°; 2-benzyl-5-chlorooxazole-4-carboxylic acid, m. 183° (decomposition); Et ester, b0.02 170-5°; acid chloride, m. 156-7°; cyano compound, m. 49-50°; aldehyde [dinitrophenylhydrazone, m. 173°; semicarbazone, m. 185° (decomposition)]; 2-(2-benzyl-5-chloro-4-oxazolyl)-5,5-dimethylthiazolidine-4-carbo-xylic acid-HCl, m. 176-7° (decomposition). By refluxing 223 mg. XVIII in 3 mL. EtOH with 40 mg. Na, the Cl was replaced by the EtO group with formation of the corresponding acid, XVIIa. Distillation of the aldehyde XIX at 0.1 mm. gave 2-phenyloxazole-4-carboxylic acid chloride, m. 107-8°, transformed by stirring with cold concentrated aqueous NH4OH to the amide. Similarly the acid chloride XVIIb was converted to the amide, m. 118-19°, rearranged by heating for a few rain. at 140° to Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 183deg;. All oxazoles found to undergo rearrangement may be formulated as 5-substituted oxazoles having a CO group in the 4-position, the general case being N:CR'.O.CR3:CCOR2 → N:CR'.O.CR2:CCOR3. Known examples of rearrangement are tabulated. Since the mol. is unstable when R3 and R2 are Et and Cl, resp., or when R3 and R2 are Cl and H, resp., it is deduced that the ethoxy aldehydes should show too great stability for successful synthesis. Cyclization of AmCONHCHCNCO2Et with P2O5 in CHCl3 gave 2-amyl-4-cyano-5-ethoxyoxazole, b0.03 98°, not reduced to the aldehyde by SnCl2 in Et2O. No 4-acetyloxazole was obtained from the MeMgI reaction product but the isolation of Et α-caproylaminoacetoacetate (dinitrophenylhydrazone, m. 166-7°) indicated oxazole ring cleavage. The dehydration of 2-phenyl-5-ethoxyoxazole-4-carboxyamide with POCl3 or the ethylation with MeCHN2 of the crude oxazolone obtained by treating BzNHCHCNCO2H with Ac2O produced 2-phenyl-4-cyano-5-ethoxyoxazole, m. 77°. The previously unknown 5-aminooxazoles were prepared thus: treatment of 7 g. BzNHCH(CN)CO2Et, m. 138°, in 125 mL. CHCl3 with 6.2 g. PCl5 gave 4.5 g. Et 2-phenyl-5-aminooxazole-4-carboxylate, m. 185°, also prepared by the action of POCl3 on Bz-NHCH(CONH2)CO2Et. Condensation of 1.18 g. H2NCH-(CO2Et)2 with 1.13 g. PhNHOEt by heating for 30 min. at 110° gave the alternative compound, formulated as 2-phenyl-4-carbethoxy-5-imidazolone, m. 275°. Similarly were prepared Et 2-benzyl-5-aminooxazole-4-carboxylate (XX), m. 124° and the corresponding 2-benzyl-4-carbethoxy-5-imidazolone, m. 254° (decomposition); 2-(1-pentenyl)-4-carbethoxy-5-aminooxazole, m. 105°; 2-amyl-4-carbethoxy-5-aminooxazole (XXa), m. 104° and the corresponding 2-amyl-4-carbethoxy-5-imidazolone., m. 230° (decomposition). On heating at 170° for 5 min., XXa was entirely converted into AmCONHCH(CN.)CO2Et, m. 83°. Heating either XX or PhCH2CONHCH(CN)CO2Et at 160-70° for 15 min. produced an equilibrium mixture with the open chain ester predominating. This same mixture was formed by heating 2-benzyl-5-ethoxyoxazole-5-carboxylic amide, probably through initial rearrangement to the aminooxazole. Stirring 35 g. NCCH2CO2CH2Ph in 40 mL. of chilled glacial AcOH with saturated aqueous NaNO2 (16.5 g.) yielded 29 g. NCC(NOH)CO2CH2Ph, m. 119°, reduced with Al-Hg to NCC(NH2)CO2CH2Ph, m. 95°, and benzoylated to NCCH(NHBz)CO2CH2Ph, m. 130°, converted by heating at 160° for 5 min. to 2-phenyl-4-carbobenzyloxy-5-aminooxazole, m. 203°. The 4-carbethoxy-5-aminooxazoles are feebly basic substances whose HCl salts dissociate readily. XXa.HCl, on boiling with ethereal EtOH gave AmCONHCH(CONH2)CO2Et, m. 150-1°, along with NH4Cl. Treatment of 1 g. XXa in 10 mL. dry Et2O at -15° with NOCl gave a low yield of Et 2-amyl-oxazole-4-carboxylate, m. 92-3°. Formylation of 15 g. BzNHCH2CN in 200 mL. HCO2Et and 100 mL. benzene by addition of NaOEt (from 2.16 g. Na) in 100 mL. benzene produced, after treatment of the

intermediate BzNHC(:CHONa)CO2H with dilute H2SO4 to pH 4, 2-phenyl-5-aminooxazole-4-carboxaldehyde (XXI), m. 172-3°, probably in the tautomeric form. Formylation of AmCONHCH2CN and distillation of the product yielded 2-amyl-oxazole-4-carboxylic acid amide, m. 154-5°, evidently by rearrangement of XXI. The action of POCl3 on Bz-NHCH(CONH2)2 and AmCONHCH(CONH2)2, m. 231°, gave 2-phenyl-5-amino-4-cyanooxazole, m. 233° (Ac derivative, m. 202-3°), and 2-amyl-5-amino-4-cyanooxazole, m. 117°. These aminooxazoles could not be reduced to aldehydes.

Saturation of 0.52 g. PhCH2CSNHCH(CN)CO2Et, m. 157°, treated in 5 mL. dry EtOH with dry HCl at -10° and the solution evaporated after 12 h. at 20° in vacuo yielded 0.5 g. 2-benzyl-4-carbethoxy-5-aminothiazole, m. 180°. OXAZOLONE SECTION. Part. I. General Chemical of Oxazolones. Preparation of 2-Oxazolin-5-ones. The reaction of Ac2O with α-acylamino acids is the most general procedure by which new oxazolones, O.CR:N.CR1R2.CO, have been prepared (substituents given): 2-Me, 4-iso-Pr, b10 60°; 2-PhCH2, 4-Me, b0.5-1.0 122-3°; 2-PhCH2, 4-iso-Pr, b0.5 115-17°; 2,4-(PhCH2)2, oil; 2-Am, 4-PhCH2, b5 135-8°; 2-(2-pentenyl), 4-PhCH2, b1.0 155-7°; 2-PhCH2, 4,4-Me2 (I), m. 59.5°; 2-Ph, 4-iso-Bu, m. 56-7°; 2-PhCH2, 4-sec-Bu, b2.0 137-9°; 2-Ph, 4,4-C5H10, m. 71°; 2-PhCH2, 4-Me, 4-PhCH:CH, m. 56-7°; 2-Ph, 4-CO2Et, m. 147-8°; 2-Am, 4-CO2Et, oil; 2-Ph, 4-(p-MeOC6H4CH2); 2-PhCH2, 4-(p-MeOC6H4CH2); and 2-PhCH2, 4-iso-Bu. Similarly, heating 100 g. BzNHCH2CO2H (II) in 300 mL. Ac2O at 100° yielded 49 g. 2-phenyl-2-oxazolin-5-one (III), m. 94-5°, the only monosubstituted oxazolone prepared by this method. By warming BzNHCHPhCH2CO2H in CHCl3 with 1 equivalent of 2-benzyl-4-methyl-5-oxazolone, a good yield of 2-phenyl-4-benzyl-5-oxazolone, m. 68-9°, was obtained. Addition of 1 g. NaNO2 in 20 mL. H2O to 3 g. of BzNHC(CONHNH2):-CHPh in 30 mL. N HCl gave α-benzamidocinnamic azide, m. 113-4° (decomposition), converted on boiling with EtOH or treatment with pyridine at room temperature to 2-phenyl-4-benzylidene-5-oxazolone (IV). Similarly, Me2C:C(NHBz)-CON3 was converted to 2-phenyl-4-isopropylidene-5-oxazolone (IVa). These type II (unsatd. substituent at the 4-position) unsatd. oxazolines are formed more readily than the above-listed type I (saturated substituent at the 4-position) saturated oxazolones to which the azide conversion could not be extended. Reduction of IV over Pd-C gave 2-phenyl-4-benzyl-5-oxazolone (V), m. 67-8°. IVa was similarly reduced in dioxane to give an oil which, treated with PhNH2 in benzene, produced Me2CHCH(NHBz)CONHPh, m. 211-2°. The possibility arose that any reagent capable of transforming an acid to its chloride might be expected to convert an α-acylamino acid to the corresponding oxazolone. Thus treatment of II in 15 mL. dioxane with 2 mL. PBr3 gave III. Similarly, 14.5 g. PhCH2CONHCMe2CO2H in 150 mL. dioxane was treated with 18 g. PBr3. The solid product suspended in dioxane and treated with slight excess of CH2N2 in ether yielded I, converted by PhCH2NH2 into PhCH2CONHCMe2CONH2, m. 122-3°. Treatment of PhCH2CHNHBzCO2H in pyridine with PBr3 likewise gave the known V. Attempts to prepare 2-benzyl-5-oxazolone from PhCH2CONHCH2CO2H gave an unstable oil, converted by PhCH2NH2 into PhCH2CONHCH2CONHCH2Ph. Conversion of PhCH:C(NHBz)CO2H into IV was effected by POCl3, SOCl2, pyridine, by ClCH2COCl and K2CO3, and by AcCl in dioxane. Oxazolones have been produced by treating PhCH2OCOCl with acylamino acids. Apart from direct dehydration, three methods are known for the preparation of type II oxazolones; the Erlenmeyer aldehydeacylglycine synthesis, the Bergmann-Stein reaction of N-(α-haloacyl)amino acids with Ac2O, and the dehydration of β-hydroxy-α-acylamino acids. In that III reacts with Me2CO in the presence of NaOAc to yield IVa in the absence of Ac2O, it is suggested that III is an intermediate in the Erlenmeyer synthesis. In the presence of a little pyridine, BzH condenses with III to produce IV. Similarly, 2-phenyl-4-propylidene-5-oxazolone, m. 88-9°, was obtained in good yield from III and EtCHO. By adding

Ac2O dropwise with stirring to 17.9 g. II and 6.1 g. fused NaOAc in 580 mL. Me2CO, refluxing for 3-4 h. at 59-62°, pouring the reaction mixture over 200 g. ice and diluting to 1500 mL. produced high yields (73%) of relatively pure 2-phenyl-4-isopropylidene-5-oxazolone, m. 98°. Condensation of II with (EtO)2CHCHO and Ac2O gave 4,4'-glyoxalidenebis(2-phenyl-5-oxazolone), m. 325° (decomposition). Though no acyl interchange in the Erlenmeyer synthesis occurs with II, the formation of 2-methyl-4-benzylidene-5-oxazolone occurs when either PhCH2CONHCH2CO2H or AmCONHCH2CO2H (VI) is refluxed with BzH in the presence of Ac2O and NaOAc. Refluxing VI (15.1 g.) with 13.1 g. AmCO2Na and 61 g. (AmCO)2O in 49 mL. Me2CO for 24 h. at 75° gave α-caproyl-amino-β,β-dimethylacrylic acid, m. 162-3°, converted by melting and heating in vacuo at 180-90° into 2-amyl-4-isopropylidene-5-oxazolone, b0.03 60-2°. By Bergmann's method, 2-methyl-4-isopropylidene-5-oxazolone (VII) and 2-methyl-4-sec-butylidene-5-oxazolone were prepared from Me2CHCH2CH(NHCOCH2Cl)CO2H and EtMeCHCH-(NHCOCH2Cl)CO2H. Carter's method was used to prepare VII by the action of Ac2O on Me2C(OMe)CHNH2CO2H. Ring opening Reactions of Oxazolones. The general reaction of oxazolones with H2O, ROH, RSH, NH3, RNH2 and RR'NH represented by O .CR:N.CR1R2.CO + HX → OCRHNCR1R2COX, suggested originally the thiazolidine-oxazolone formulation of penicillin. Comparison of the reactivity of V with that of IV showed the former to be rapidly hydrolyzed by 2N aqueous acid or alkali under conditions not affecting the latter. V reacts with ROH more rapidly than III. In the presence of NaOMe or PhCH2NMe3-OH, IVa was converted quant. to Me2C:C(BzNH)CO2Me, m. 130-1°. The methanolysis of 2-benzyl-4-p-methoxybenzyl-5-oxazolone in dry absolute MeOH yielded (N-phenylacetyl-p-methoxyphenylalanyl)-p-methoxyphenylalanine, m. 199-200°. The formation of the dipeptide may be due to an "ortho-ester" reaction with the imino-ether form of the oxazolone. Reaction of PhCH2SH with III and I yielded benzyl hippurate, m. 101-2° and Me2CHCH(NHCOCH2Ph)COSCH2Ph, m. 138.5°. Almost all types of oxazolones react with PhCH2NH2 to form α-acylaminoacyl-benzylamides. The reaction of V with d-MePhCHNH2 in dry dioxane was followed polarimetrically and at constant rotation, produced N-benzoylphenylalanine-d-N-α-phenylethylamide, m. 178-80°, [α]D23 28.5° (c 1, dioxane). The strongly enolyzed 2-phenyl-4-carbethoxy-5-oxazolone formed a salt with PhCH2NH2, converted on heating in xylene to the benzylamide, m. 132°. The reaction of PhNH2.HCl with III and 2-benzyl-4-sec-butyl-5-oxazolone gave the normal anilide and the corresponding acid. Reaction of V and 2-phenyl-4-isobutyl-5-oxazolone with L-HSCH2CH-(NH2)CO2Me produced the normal amides, m. 128-9°, and 131-5°, resp., the NH2 group taking precedence over the SH group in the condensation. The action of N2H4 on oxazolones has been clarified. The addition of 18 g.-phenyl-4-methyl-5-oxazolone to excess 60% N2H4.H2O in EtOH and heating to 50-60° for 30 min. gave 17.5 g. benzoylalanine hydrazide, m. 142-4°; benzylidene derivative, m. 193-4°. Treatment of IV with N2H4.H2O also gave the normal hydrazide, PhCH:C(NHBz)CONHNH2, m. 113-14°, converted by heating the corresponding azide in xylene to 2-oxo-4-benzylidene-6-phenyl-1,3,5-oxadiazine, m. 174° (decomposition). Conversion of Me2C:C(NHBz)CON3 similarly produced 2-oxo-4-isopropylidene-6-phenyl-1,3,5-oxadiazine, m. 166-8°. A mixture of 5 g. IV, 10 mL. N2H4.H2O and 3 mL. EtOH was refluxed for 30 min. yielding 4-benzamido-3-phenyl-5-pyrazolidone, m. 228-9°, identical with the product formed by refluxing PhCH:C(NHBz)CONHNH2 (VIII), m. 157-8°, which N2H4.H2O for 30 min. Similarly, the hydrazide Me2C:C(NHBz)CONHNH2, m. 192-4°, was converted into 3,3-dimethyl-4-benzoylamino-5-pyrazolidine, m. 106-8°. The hydrazide VIII was boiled in N NaOH and the sparingly soluble salt on acidification gave 6-hydroxy-5-benzyl-3-phenyl-1,2,4-triazine, m. 175-6°; Ac derivative, 187-8°. Oxidation of XIII with K3Fe(CN)6 produced N,N'-bis(α-benzoylaminocinnamoyl)hydrazine, m. 265°,

together with a substance, m. 186-7°, with the probable structure PhCH:C.CH(OH).NBz.C-(:CHPh).CH(OH).NBz, forming PhCH2CH(NHBz)-(CO2H) on alkaline hydrolysis. REACTIONS OF TYPE II OXAZOLONES: Some reactions involving the double bond in type II oxazolones have been discovered. Treatment of IV in dry dioxane with 2 mol CH2N2 in dry Et2O at 0° and allowing the solution to stand overnight at room temperature gave product, C17H13O2N, m. 142-3°. Addition of liquid NH3 to IVa with shaking and cooling in solid CO2 gave a small yield of basic product, C12H17O2N3, m. 162-6°, probably by addition of 2 mol NH3. Addition of H2S and RSH to the double bond has been studied in connection with various syntheses of penicillamine. The addition, of 136 g. IVa in 675 mL. dry benzene to 3.38 g. Na in 675 mL. of chilled dry MeOH and 76.5 mL. PhCH2SH produced Me2CC(NHBz)CO2Me, m. 137-8°, and Me2C(SCH2Ph)CH(NHBz)CO2Me, m. 66-7°. The addition probably takes place after ring opening, since the oxazolone can be replaced by an acrylic ester. Similarly, IV under like conditions, gave PhCH(SCH2Ph)CH-(NHBz)CO2Me, m. 164°. There is no evidence of direct addition of PhCH2SH to the double bond. Addition of H2S to IVa and VII in the presence of Et3N yielded Me2C(SH)CH(NHBz)COSH and Me2C(SH)CH(NHAc)COSH, resp. The initial step is probably the addition of H2S to the double bond. Anhydrous MeOH saturated with H2S at 0° treated with IVa gave 2,5,5-trimethyl-2-thiazoline-4-carboxylic acid, b25 120°; picrate, m. 159°, probably formed by addition, followed by displacement. IV similarly yielded 2-phenyl-5,5-dimethyl-2-thiazoline-4-carboxylic acid, m. 124-6°. IVa was apparently converted by treatment with alc. NaSH to 2-phenyl-4-isopropylidene-5-thiazolone, m. 100.5-101.5°. The reactivity of the Me groups in IVa is sufficient to permit condensation reactions with BzH to produce 2-phenyl-4-benzylideneisopropylidene-5-oxazolone, m. 135°. A mixture of stereoisomers, m. 134-6°, was produced by heating a mixture of 35.8 g. BzNHCH2CO2H, 32 g. PhCH:CHAc, 15 g. of fused NaOAc and 50 mL. Ac2O for 3 h. at 100°. IVa is a pseudo-acid and exhibits weak violet fluorescence in Et3N. On addition of NaOMe to IVa in MeOH, the initial intense blue-violet fluorescence in UV light due to the presence of the propenyl-oxazole soon disappears with the formation of Me2C:C(NHBz)CO2Me by ring opening. Miscellaneous REACTIONS OF OXAZOLONES. Excess PhMgBr was added to 6.0 g. 2-phenyl-4-methyl-5-oxazolone in Et2O and after refluxing for 6 h. the reaction product was hydrolyzed and extracted with Et2O, yielding 4.6 g. 1,1-diphenyl-2-benzoylamino-propanol, m. 192-3°. With AgClO4 in benzene, III in EtOH gave a complex, m. 146° (decomposition). A similar crystalline compound, m. 172° (decomposition) was formed with 2-benzyl-4-methyl-5-oxazolone (IX). Formylation of 2,4-diphenyl-5-oxazolone apparently produced a stabilized enolic form, PhC:N.CPh:COH.O, m. 110°. Oxidation of 2-phenyl-4-isobutyl- and 2-phenyl-4-benzyl-5-oxazolones with Hg(OAc)2 gave the corresponding 4,4'-bisoxazolones, m. 138-42°, and 201-202.5°, resp. PSEUDO-OXAZOLONES. According to the method of Bergmann, 12 g. PhCHBrCONHCH2CO2H was added to 5 mL. dry pyridine and 100 mL. Ac2O and after 2.5 h. at 0° was poured over ice. The solid product was dried over NaOH and crystallized from warm MeOH by cooling to -50°, yielding 64% of 2-benzylidenepseudooxazolone (2-benzylidene-3-oxazolin-5-one), m. 92-4°, hydrolyzed by 0.5N HCl in acetone to PhCH2-CONH2, m. 153-7°. An attempt to prepare 2-benzyl-4-methylene-5-oxazolone by Bergmann's method from Ph-CHClCONHCHMeCO2H gave the potent skin irritant 2-benzylidene-4-methylpseudo-5-oxazolone (X), m. 105-115°, hydrolyzed by aqueous acetone to PhCH2CONH2 and AcCO2H, suggesting that the pseudooxazolones are intermediates in the Bermann synthesis of type II oxazolones and that, in general, the latter are in dynamic equilibrium with the pseudooxazolones. In an attempt to use pseudooxazolones for the thiazolidine-oxazolone structure suggested for penicillin, Br was added to V and the product condensed with penicillamine (XI) in the presence of AcOK and AcOH. The low order of activity noted was probably due to

BrCH2COCO2H which has an activity of 6 units per mg. against Gram-pos. organisms. X (1 g.) in 40 mL. pure AcOEt was hydrogenated at several atmospheric pressure in the presence of 2 g. active Raney Ni to IX, suggesting that the thiazolidine-oxazolone structure might be accessible by reduction of the corresponding pseudooxazolone. Ice-cold pyridine (20 mL.) in 65 mL. Me2CO was mixed with 1 g. (EtO)2CHCH(NHCOCHBrPh)CO2H and after 3 h., the mixture was poured over crushed ice, extracted with CHCl3, washed with aqueous NaHCO3, dried by passage through acid-washed Al2O3, and the filtrate was evaporated, yielding 4.8 g. oily 2-benzylidene-4-(diethoxymethyl)pseudo-5-oxazolone, which failed to condense with XI. In another attempt, (EtO)2CHCH(NHCOCHClPh)CO2Me was condensed with XI to give α-Me α-chlorobenzylpenicilloate (XII). On treatment of crude XII (5.2 g.) with a mixture of 10.8 g. pyridine and 35.2 mL. Ac2O with shaking and cooling, a dark brown gum was formed, which, crystallized from Et2O at -50°, gave a "dehydropenicillin" (XIII), C16H16O4N2S, m. 90-5° (decomposition). Addnl. information in printed abstract

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=> s oxazoline and polymerization inhibit?
         10405 OXAZOLINE
        376602 POLYMERIZATION
       2157778 INHIBIT?
          6011 POLYMERIZATION INHIBIT?
                 (POLYMERIZATION(W)INHIBIT?)
L9            7 OXAZOLINE AND POLYMERIZATION INHIBIT?

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YOU HAVE REQUESTED DATA FROM 7 ANSWERS - CONTINUE? Y/(N):y

L9   ANSWER 1 OF 7  CAPLUS  COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER:         2006:1033648  CAPLUS
DOCUMENT NUMBER:          145:400523
TITLE:                    Solid additive composition and method thereof
INVENTOR(S):              Burrington, James D.; George, Herman F.; Byfleet,
                          William D.; Baker, Mark R.; Hurley, Susie; Sumiejski,
                          James L.; Ineman, Jennifer M.
PATENT ASSIGNEE(S):       The Lubrizol Corporation, USA
SOURCE:                   PCT Int. Appl., 22pp.
                          CODEN: PIXXD2
DOCUMENT TYPE:            Patent
LANGUAGE:                 English
FAMILY ACC. NUM. COUNT:   1
PATENT INFORMATION:

     PATENT NO.          KIND   DATE        APPLICATION NO.        DATE
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     WO 2006105025        A1    20061005    WO 2006-US11121        20060327
         W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
            CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
            GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR,
            KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX,
            MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE,
            SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC,
            VN, YU, ZA, ZM, ZW
         RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE,
            IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ,
            CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH,
            GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY,
            KG, KZ, MD, RU, TJ, TM
     US 20060229215        A1    20061012    US 2005-92403          20050329
     AU 2006230103         A1    20061005    AU 2006-230103         20060327
     CA 2603007            A1    20061005    CA 2006-2603007        20060327
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EP 1877527		A1	20080116	EP 2006-739737	20060327
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR					
JP 2008534746		T	20080828	JP 2008-504228	20060327
IN 2007DN07685		A	20071109	IN 2007-DN7685	20071008
CN 101184831		A	20080521	CN 2006-80018527	20071127
PRIORITY APPLN. INFO.:				US 2005-92403	A 20050329
				WO 2006-US11121	W 20060327

AB An additive composition comprises (A) an additive comprising a nitrogen-containing detergent, a fatty acid based friction modifier, or a mixture thereof and (B) a solid organic matrix material where the additive composition is a solid that melts in the range of .apprx.25 to .apprx.200°. A method to enhance performance of a functional fluid, especially a fuel composition or power transmission fluid of a vehicle powered by an internal combustion engine, comprises adding a performance-enhancing amount of the additive composition to the functional fluid.

REFERENCE COUNT: 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 2 OF 7 CAPLUS COPYRIGHT 2009 ACS on STN

ACCESSION NUMBER: 2006:322508 CAPLUS
DOCUMENT NUMBER: 144:351671
TITLE: Optically clear stabilized polycarbonate-polyester compositions
INVENTOR(S): Juikar, Vishvajit Chandrakant; Kannan, Ganesh; Wit, Gerrit De
PATENT ASSIGNEE(S): General Electric Company, USA
SOURCE: U.S. Pat. Appl. Publ., 16 pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
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US 20060074202	A1	20060406	US 2004-952613	20040929
WO 2006044087	A1	20060427	WO 2005-US33320	20050915
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
EP 1797136	A1	20070620	EP 2005-846423	20050915
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR				
CN 101065433	A	20071031	CN 2005-80040770	20050915
JP 2008514756	T	20080508	JP 2007-533564	20050915
PRIORITY APPLN. INFO.:			US 2004-952613	A 20040929
			WO 2005-US33320	W 20050915

AB A stabilized thermoplastic resin composition comprises structural units derived from at least one substituted or unsubstituted polycarbonate, at least one substituted or unsubstituted polyester, a cyclic iminoether-containing compound,

and an additive. In another embodiment, a stabilized thermoplastic resin composition comprises structural units derived from at least one substituted or unsubstituted polycarbonate, at least one substituted or unsubstituted polyester, a cyclic iminoether-containing compound, a quencher, and an additive.

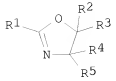
The composition has improved optical properties, thermal properties and stability. Thus, a composition comprising Lexan polycarbonate (75), cyclohexanedimethanol-ethylene glycol-terephthalic acid copolymer (25%), an oxazoline derivative (0.1% based on the polymer blend), and phosphoric acid (50 ppm) was extruded at 270°, a feed rate of 15 kg/h, and a screw speed of 300 rpm. The composition was pelletized, dried for at least 4 h at 100°, and injection molded at 280° to obtain a test sample showing a yellowness index of 1.56, a haze of 1.22%, and a transmission of 89.9% (ASTM D-1003).

L9 ANSWER 3 OF 7 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2005:472105 CAPLUS
DOCUMENT NUMBER: 143:8161
TITLE: Method for the esterification of alcohols with olefinically unsaturated carboxylic acids
INVENTOR(S): Glos, Martin
PATENT ASSIGNEE(S): Clariant G.m.b.H., Germany
SOURCE: PCT Int. Appl., 20 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005049544	A1	20050602	WO 2004-EP12790	20041111
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
DE 10354652	A1	20050707	DE 2003-10354652	20031122
AU 2004291298	A1	20050602	AU 2004-291298	20041111
CA 2546819	A1	20050602	CA 2004-2546819	20041111
EP 1687251	A1	20060809	EP 2004-797820	20041111
EP 1687251	B1	20090318		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS				
BR 2004016734	A	20070116	BR 2004-16734	20041111
CN 1902155	A	20070124	CN 2004-80030595	20041111
JP 2007511561	T	20070510	JP 2006-540260	20041111
ES 2320227	T3	20090520	ES 2004-797820	20041111
MX 2006005674	A	20060817	MX 2006-5674	20060519
US 20070149803	A1	20070628	US 2006-580384	20060522

PRIORITY APPLN. INFO.: DE 2003-10354652 A 20031122
WO 2004-EP12790 W 20041111

OTHER SOURCE(S): MARPAT 143:8161
GI



I

AB The invention relates to a method for producing esters from alcs. and olefinically unsatd. carboxylic acids by reacting an alc. with an olefinically unsatd. carboxylic acid or a reactive derivative thereof, in the presence of between 1 ppm and 1 weight % oxazoline I in relation to the weight of the reaction mixture of alc. and olefinically unsatd. carboxylic acid/carboxylic acid derivative, R1, R2, R3, R4 and R5 representing hydrogen or branched, linear, cyclical, saturated or unsatd. hydrocarbon radicals containing up to 25 C atoms that can be substituted by heteroatoms, and R1, R2, R3, R4 and R5 being the same or different to prevent formation of polymer on surfaces in reactor.
REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 4 OF 7 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1989:553220 CAPLUS
DOCUMENT NUMBER: 111:153220
ORIGINAL REFERENCE NO.: 111:25533a,25536a
TITLE: Purification of unsaturated carboxylic acid isocyanatoalkyl esters by distillation
INVENTOR(S): Abe, Tetsuo; Yokoo, Hidejiro; Wakasa, Masami
PATENT ASSIGNEE(S): Showa Rodia Kagaku Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 01042463	A	19890214	JP 1987-198157	19870810
JP 07103085	B	19951108		
PRIORITY APPLN. INFO.:			JP 1987-198157	19870810

OTHER SOURCE(S): MARPAT 111:153220
AB The title esters, useful as monomers, are purified by distillation in the presence of ≥1 compound selected from phenothiazine (I), alkylphenols, hydroquinone, alkylhydroquinones, p-MeOC6H4OH, tannic acid, and anthraquinone and ≥1 compound selected from Et2NCH2CH2OH (II), N-nitroso-N-arylhydroxylamine NH4 salts, N-nitroso-N-propylurethane, H2NNHCH2CH2OH, and C6H4(NO2)2 to prevent popcorn polymerization CH2:CMeCO2H (320 g) was gradually added to mixture of 300 g 2-oxazolidinone, I, and toluene while bubbling with HCl over 60 min, and the reaction mixture was further stirred at 60° for 30 min, and then heated at 80° while bubbling with COCl2. After distilling off toluene, 230 g reaction mixture containing CH2:CMeCO2CH2CH2NCO (III) was distilled with II under 10-12 mmHg while adding 50 g reaction mixture containing II dropwise to give 108 g III, vs. formation of polymers preventing distillation for a control without addition of II.

L9 ANSWER 5 OF 7 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1989:477514 CAPLUS
DOCUMENT NUMBER: 111:77514

ORIGINAL REFERENCE NO.: 111:13055a,13058a
TITLE: Purification of unsaturated carboxylic acid isocyanatoalkyl esters by distillation
INVENTOR(S): Abe, Tetsuo; Yokoo, Hidejiro; Nozawa, Kaneo
PATENT ASSIGNEE(S): Showa Rodia Kagaku Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 01042461	A	19890214	JP 1987-198155	19870810
JP 07049413	B	19950531		

PRIORITY APPLN. INFO.: JP 1987-198155 19870810
OTHER SOURCE(S): MARPAT 111:77514

AB The title esters, useful as monomers, are purified by distillation under continuous or intermittent addition of nitrite esters in the presence of Sn(2+) and/or Fe(2+) compds. to prevent popcorn polymerization CH2:CMeCO2H (320 g) was gradually added to a solution of 300 g 2-oxazolidinone in toluene containing phenothiazine while bubbling with HCl at 60° over 60 min, and the reaction mixture was further bubbled with HCl at 60° for 30 min, and then heated at 80° while bubbling with COCl2. After distilling off toluene, 230 g product containing CH2:CMeCO2CH2CH2NCO (I) was distilled with SnCl2 and the HNO2 ester (II) of HOCH2CH2OCH2CH2OBu under dropwise addition of 50 g product containing II to give 115 g I. When the reaction product was distilled without addition of SnCl2 and II, granules of polymerized matter were formed at the upper part of the distillation tower and polymer beads grew in the reaction mixture

L9 ANSWER 6 OF 7 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1989:457070 CAPLUS
DOCUMENT NUMBER: 111:57070
ORIGINAL REFERENCE NO.: 111:9675a,9678a
TITLE: Purification of unsaturated carboxylic acid isocyanatoalkyl esters by distillation
INVENTOR(S): Abe, Tetsuo; Yokoo, Hidejiro
PATENT ASSIGNEE(S): Showa Rodia Kagaku Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 01042462	A	19890214	JP 1987-198156	19870810
JP 07049414	B	19950531		

PRIORITY APPLN. INFO.: JP 1987-198156 19870810
OTHER SOURCE(S): MARPAT 111:57070

AB Unsatd. carboxylic acid isocyanatoalkyl esters, useful as monomers, are purified by distillation under continuous or intermittent feeding of cupferrons dissolved in glycols to prevent popcorn polymerization An aqueous solution of 150 g 2-isopropenyl-2-oxazoline, a solution of 200 g COCl2 in CH2Cl2, and an aqueous NaOH solution were simultaneously added to CH2Cl2 at ≤15°, and the reaction mixture was further stirred for several mins and separated After distilling off CH2Cl2 from the organic layer, the product

was distilled with cupferron (I) dissolved in ethylene glycol (II) under decreased pressure while continuously adding a solution of I in II to give 181 g CH2:CMeCO2CH2CH2NCO, vs. formation of polymerized matter preventing distillation for a control without addition of I.

L9 ANSWER 7 OF 7 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 1961:105947 CAPLUS
DOCUMENT NUMBER: 55:105947
ORIGINAL REFERENCE NO.: 55:19960a-e
TITLE: 4,4-Dialkyl-2-vinyl- and 4,4-dialkyl-2-isopropenyloxazolines and 5,6-dihydro-4H-1,3-oxazines and their spirans
INVENTOR(S): Luskin, Leo Samuel; De Benneville, Peter L.
PATENT ASSIGNEE(S): Rohm & Haas Co.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1067437		19591022	DE	

AB Acryloyl halides or their α-alkyl derivs. were treated with excess alkanolamines, such as 2-amino-2-methylpropanol (I), 3-amino-3-methylbutanol (II), 2-amino-2-methyl-1-decanol (III), or 2-amino-2-methyl-1-octanol (IV) and the amides formed heated at 170-230° in the presence of a strong mineral acid and a polymerization inhibitor to give the title oxazolines or oxazines. The products were fungicides and could be polymerized or copolymerized. The fungicidal action was tested. The infrared spectra of the compds. prepared were discussed. E.g., I 105 and C6H6 50 was cooled at 10-15°, treated with CH2:CMeCOCl (V) 104.5 in C6H6 100 parts over 2 hrs. at 10-40°, the mixture stirred 4 hrs. without cooling, the precipitate filtered off, washed with C6H6, the filtered solution and the washings combined, evaporated, and distilled in the presence of p-hydroxydiphenylamine to give 90% N-(1,1-dimethyl-2-hydroxyethyl)methacrylamide, b0.15 92-105°, n25D 1.4785). The amide, p-hydroxydiphenylamine 0.5, and H2SO4 0.5 was heated at 175-230° 1.5 hrs. and the mixture 24.5 parts of H2O and oxazoline distilled simultaneously through a short column and redistd. to give 60% 2-isopropenyl-4,4-dimethyloxazoline, b24 58-9°, n25D 1.453, an effective fungicide and a monomer for polymerization and copolymerization. Similarly, II and V gave N-(1,1-dimethyl-3-hydroxypropyl)methacrylamide, b0.13 95-110°, and 2-isopropenyl-4,4-dimethyl-5,6-dihydro-4H-1,3-oxazine, b13 58-65°, n25D 1.4558. I and CH2:CHCOCl gave oily N-(1,1-dimethyl-2-hydroxyethyl)acrylamide and 2-vinyl-4,4-dimethyloxazoline, b32 54°, n25D 1.4356). CH2:CHCOCl and III gave oily N-(1-methyl-1-hexyl-2-hydroxyethyl)acrylamide and 2-vinyl-4-methyl-4-hexyloxazoline, b13 78-90°, n25D 1.4533). IV and V gave N-(1-methyl-1-octyl-2-hydroxyethyl)methacrylamide and 2-isopropenyl-4-methyl-4-octyloxazoline, b25 72-5°, n25D 1.4482. V and 1-amino-1-(hydroxymethyl)cyclohexane gave N-[1-(hydroxymethyl)cyclohexyl]methacrylamide and 2-isopropenyl-4-spiro(cyclohexaneoxazolidine), b12 90-110°, n25D 1.4853, which could be used for treatment of leather and for polymerization.

=> E GLOS MARTIN/AU 25
E1 1 GLOS L/AU
E2 1 GLOS M/AU
E3 39 --> GLOS MARTIN/AU

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E5            2     GLOS MICHAEL/AU
E6            3     GLOS MIROSLAV/AU
E7            4     GLOS P/AU
E8            1     GLOS RAINER/AU
E9            1     GLOS S/AU
E10           1     GLOS SABRINA/AU
E11           5     GLOS STEFAN/AU
E12           2     GLOS T/AU
E13           2     GLOS U/AU
E14           1     GLOSAFATTO C V L/AU
E15           1     GLOSAUER EVA M/AU
E16          11     GLOSAUER OTTO/AU
E17           9     GLOSBY A A/AU
E18           1     GLOSCH BERNADETT/AU
E19           4     GLOSCH H/AU
E20           1     GLOSCH HARTMUT/AU
E21           3     GLOSCOW ELEANOR J/AU
E22           6     GLOSE CHRISTOPHER R/AU
E23           4     GLOSE CHRISTOPHER RAYMOND/AU
E24           4     GLOSE KEN/AU
E25           3     GLOSE KENNETH H/AU

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           39 "GLOS MARTIN"/AU
L10        40 ("GLOS M"/AU OR "GLOS MARTIN"/AU)

=> s l4 and l10
L11         2 L4 AND L10

=> d l11 ibib abs 1-
YOU HAVE REQUESTED DATA FROM 2 ANSWERS - CONTINUE? Y/(N):y

L11  ANSWER 1 OF 2  CAPLUS  COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER:         2005:472105  CAPLUS
DOCUMENT NUMBER:          143:8161
TITLE:                    Method for the esterification of alcohols with
                          olefinically unsaturated carboxylic acids
INVENTOR(S):              Glos, Martin
PATENT ASSIGNEE(S):       Clariant G.m.b.H., Germany
SOURCE:                   PCT Int. Appl., 20 pp.
                          CODEN: PIXXD2
DOCUMENT TYPE:            Patent
LANGUAGE:                 German
FAMILY ACC. NUM. COUNT:   1
PATENT INFORMATION:

     PATENT NO.          KIND   DATE        APPLICATION NO.        DATE
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     WO 2005049544        A1    20050602    WO 2004-EP12790        20041111
         W:  AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
             CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,
             GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,
             LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO,
             NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ,
             TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
         RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
             AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,
             EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO,
             SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
             NE, SN, TD, TG
     DE 10354652          A1    20050707    DE 2003-10354652       20031122
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AU 2004291298	A1	20050602	AU 2004-291298		20041111
CA 2546819	A1	20050602	CA 2004-2546819		20041111
EP 1687251	A1	20060809	EP 2004-797820		20041111
EP 1687251	B1	20090318			
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS					
BR 2004016734	A	20070116	BR 2004-16734		20041111
CN 1902155	A	20070124	CN 2004-80030595		20041111
JP 2007511561	T	20070510	JP 2006-540260		20041111
ES 2320227	T3	20090520	ES 2004-797820		20041111
MX 2006005674	A	20060817	MX 2006-5674		20060519
US 20070149803	A1	20070628	US 2006-580384		20060522
PRIORITY APPLN. INFO.:			DE 2003-10354652	A	20031122
			WO 2004-EP12790	W	20041111

OTHER SOURCE(S): MARPAT 143:8161
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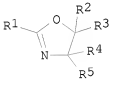

I

AB The invention relates to a method for producing esters from alcs. and olefinically unsatd. carboxylic acids by reacting an alc. with an olefinically unsatd. carboxylic acid or a reactive derivative thereof, in the presence of between 1 ppm and 1 weight % oxazoline I in relation to the weight of the reaction mixture of alc. and olefinically unsatd. carboxylic acid/carboxylic acid derivative, R1, R2, R3, R4 and R5 representing hydrogen or branched, linear, cyclical, saturated or unsatd. hydrocarbon radicals containing up to 25 C atoms that can be substituted by heteroatoms, and R1, R2, R3, R4 and R5 being the same or different to prevent formation of polymer on surfaces in reactor.
REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2009 ACS on STN
ACCESSION NUMBER: 2000:402279 CAPLUS
DOCUMENT NUMBER: 133:207839
TITLE: Aza-bis(oxazolines): New Chiral Ligands for Asymmetric Catalysis
AUTHOR(S): Glos, Martin; Reiser, Oliver
CORPORATE SOURCE: Institut fuer Organische Chemie, Universitaet Regensburg, Regensburg, D-93040, Germany
SOURCE: Organic Letters (2000), 2(14), 2045-2048
CODEN: ORLEF7; ISSN: 1523-7060
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 133:207839
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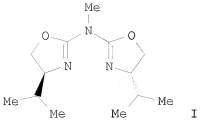

I

AB Aza-bis(oxazolines), e.g. I, are introduced as chiral ligands for asym. catalysis combining the advantages of easy availability of bis(oxazolines) and backbone variability of aza-semicorrins. The title ligands could be attached to a polymeric support, which allowed for the development of easily recoverable copper(I)-catalysts for asym. cyclopropanation reactions.

REFERENCE COUNT: 71 THERE ARE 71 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT